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JOURNAL

OF

THE CHEMICAL SOCIETY.

I.—*A Synthetic Fat containing a Methylglucoside Residue.*

By James Colquhoun Irvine and Helen Simpson Gilchrist.

It is remarkable that, with the possible exception of certain varieties of starch which contain combined palmitic acid (Taylor and Nelson, *J. Amer. Chem. Soc.*, 1920, **42**, 1726), no natural compounds appear to have been described in which the acyl residues characteristic of fats substitute the hydroxyl groups of carbohydrates. On the other hand, numerous synthetical fats are now known in which sugar residues function as the alcohol component and the series of compounds prepared by Zemplén (*Ber.*, 1915, **48**, 915) may be cited in illustration. This worker was the first to synthesise fats of the type represented by pentastearyl and pentapalmityl glucose, and, at a later date, the list was extended by Hess and Messner (*Ber.*, 1921, **54**, [*B*], 499), who succeeded in preparing hendecapalmityl raffinose and other examples showing notably high molecular weights. The pioneer in this field was, however, Berthelot, who studied the compounds formed when glucose and mannitol are esterified with palmitic, stearic, and oleic acids respectively (*Ann. Chim. Phys.*, 1856, [iii], **47**, 323; 1860, [iii], **60**, 93).

Taking into consideration the properties of these compounds and the facilities available seventy years ago, it is remarkable that Berthelot was able to show that the direct condensation with the acid component of a natural fat involved, as a supplementary reaction, internal dehydration of the carbohydrate molecule. Thus, he prepared a mannitan dipalmitate, distearate, and dioleate from mannitol, whilst a distearate of anhydro-glucose was obtained from the corresponding sugar. No structural formulæ could, of course, be assigned to these compounds, but the subject was revived in 1919 when Lapworth and Pearson (*Biochem. J.*, 1919, **13**, 296) showed that compounds similar to, if not identical with, those described by Berthelot are obtained when mannitol is heated with

either olive oil or stearin in the presence of small quantities of sodium ethoxide. In both cases, mixtures of compounds were produced and, owing to the formation of anhydrides, the fully acylated mannitol was not obtained. On the evidence of analysis, the "mannitol olive oil" consisted mainly of mannitan dioleate and *iso*mannide dioleate, and the corresponding stearates were produced when olive oil was replaced by stearin. The formation of mannitol fats of this type involves the liberation of the equivalent amount of glycerol, so that the synthesis may be regarded as a special case of the general reaction developed by Purdie in which ester groups are interchanged by the agency of sodium alkyloxides (T., 1887, **51**, 627).

The extension of the research on structural lines was allocated to us by the Food Investigation Board, and the results obtained are of considerable interest in carbohydrate chemistry. In view of future developments, it is of importance that both the composition and constitution of these carbohydrate fats should be determined, and accordingly we have in the first instance effected the condensation of olive oil with α-methylglucoside. In selecting the latter compound, several factors were taken into account. The glucoside consists of one stereochemical form and, as it contains no reducing group, is unaffected by the alkali used in the condensation. Further, carbohydrate fats of this complexity are non-volatile and either fail to crystallise or do so only imperfectly, so that the preparation of reliable analytical samples is difficult. Moreover, in view of their high molecular weights, carbon and hydrogen estimations fail to discriminate between closely-related compounds, a fact recognised by Lapworth and Pearson, who supplemented combustion analyses by determination of the hydroxyl content and of the percentage amount of combined acid in their products. The presence of a methoxyl group in the synthetic fat based on methylglucoside furnishes, however, an additional analytical factor which varies greatly according to the number of oleyl residues which enter the sugar chain.

We have shown that when α-methylglucoside is heated with olive oil in the presence of sodium alkyloxides, a definite reaction takes place and only one carbohydrate fat is produced. A single oleyl residue enters the glucoside chain to give *α-methylglucoside mono-oleate*, the equivalent proportion of glycerol being thereby liberated. When, however, the temperature exceeded a fixed limit a second reaction ensued which involved internal dehydration of the carbohydrate component. Under these conditions the essential product consisted of *anhydro-methylglucoside mono-oleate*. The configuration of α-methylglucoside evidently creates marked resistance to ester-

ification with oleic acid, although two such residues can be introduced into glucose and mannitol. Attempts to increase the substitution in the glucoside were unsuccessful, either by increasing the proportion of olive oil used in the reaction or by repeating the condensation with a mixture of olive oil and anhydro-methylglucoside mono-oleate. Although the products in each case were apparently homogeneous, they were shown to consist of mixtures of the original materials. As a result of numerous experiments, it has been proved that only one oleyl residue can be introduced, despite variations in the conditions and in the proportions of oil and glucoside used. If the glucoside is present in excess, it is found in the aqueous layer after distillation of the glycerol in steam; if the oil is in excess, a mixture of olive oil and anhydro-methylglucoside mono-oleate results which is extremely difficult to separate. The oleate is soluble in absolute alcohol, whilst olive oil is insoluble, but the mixture of oil, oleate, and alcohol forms a homogeneous system. In practice, therefore, it was found advisable to use sufficient olive oil to introduce only one oleyl residue and to use a small excess of methylglucoside. Any free glucoside present at the end of the reaction could easily be removed by washing the ethereal solution of the product with water.

As already stated, the normal reaction between olive oil and methylglucoside is succeeded by loss of a molecule of water, and the ultimate product is not methylglucoside mono-oleate, but an anhydride. This conclusion was drawn after study of the following results. In several different preparations, the methylglucoside fat was isolated, and was shown to be a uniform compound of constant composition. Some typical results may be quoted below.

Composition of Methylglucoside Fat obtained in Different Preparations.

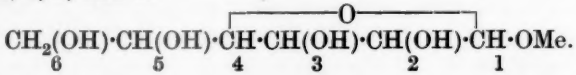
No. of preparation.	Carbon.	Hydrogen.	Methoxyl.	$[\alpha]_D^{20°}$ in chloroform.
I.	68·31	10·08	6·06	+38·55°
II.	68·11	10·37	—	38·22
III.	68·15	10·15	6·1	—
IV.	68·11	10·37	—	38·21

In the preparations referred to above, the condensation of the glucoside and olive oil was completed by heating at 220°/10 mm., but if the heating be minimised either by curtailing the time or by reducing the temperature, no internal dehydration takes place and the normal product, *methylglucoside mono-oleate*, results. This, in turn, although stable at 140°, is converted into anhydro-methylglucoside mono-oleate by heating at 220°/12 mm. The isolation of the normal compound and its subsequent dehydration therefore prove that there are two distinct reactions to be considered. The

first and primary reaction is that of condensation, the second, which follows immediately and at the same temperature, that of dehydration.

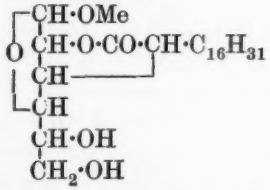
Constitution of Anhydro-methylglucoside Mono-oleate.

Regarding the constitution of such a compound, two possibilities are open. If the formula for methylglucoside be written as under, it is evident that the oleyl group may occupy any one of the positions 2, 3, 5, and 6.

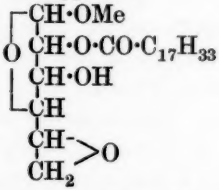


Moreover, on the one hand the formation of the anhydro-linking may be due to the elimination of a molecule of water between one hydroxyl group of the glucoside chain and a hydrogen atom of the oleyl residue; on the other hand, dehydration may occur between two hydroxyl groups of the sugar chain. Selecting an arbitrary position for the oleyl group, the constitution may be referred to one of two types and, disregarding obvious isomerism, these are represented by the following formulæ :

Type A.



Type B.



Discrimination between the two types can be effected by methylation as, if the oleyl group is intact, only one methoxyl group can be introduced as a maximum. For this purpose, a neutral reagent is necessary, and accordingly we submitted anhydromethylglucoside mono-oleate to the silver oxide reaction.

It was found that repeated methylation of the methylglucoside fat gave a pale yellow, fairly mobile oil which on examination proved to be *monomethyl anhydromethylglucoside mono-oleate*, thus showing that the anhydro-ring is formed by elimination of water between two hydroxyl groups in the carbohydrate chain, and that the oleyl residue takes no part in its formation. This excludes type A and limits attention to type B. Obviously, the monomethylated compound, obtained as above described, will be one of twelve isomerides according to (*a*) the position of the oleyl residue, and (*b*) the hydroxyl groups involved in forming the anhydro-ring. These possibilities are illustrated below, the figures within the columns indicating the positions in the sugar chain :

No. of isomeride.	Position of oleyl residue.	Position of methyl groups.	Position of anhydro-linking.	No. of isomeride.	Position of oleyl residue.	Position of methyl groups.	Position of anhydro-linking.
I.	2	1 : 6	3 : 5	VII.	5	1 : 6	2 : 3
II.	2	1 : 5	3 : 6	VIII.	5	1 : 3	2 : 6
III.	2	1 : 3	5 : 6	IX.	5	1 : 2	3 : 6
IV.	3	1 : 6	2 : 5	X.	6	1 : 5	2 : 3
V.	3	1 : 5	2 : 6	XI.	6	1 : 3	2 : 5
VI.	3	1 : 2	5 : 6	XII.	6	1 : 2	3 : 5

Before developing the structural question further, it may be mentioned that at this stage of the research much complicated work was undertaken which led to no definite result. This was due to the fact that when the methylated compound was heated under a pressure of 0·10 mm., it boiled without apparent decomposition, giving two main fractions (1) b. p. 198—203°/0·10 mm. and (2) b. p. 220—228°/0·10 mm. A detailed examination of these eventually showed that they were decomposition products, formed by a species of " cracking," but still retaining methoxyl groups.

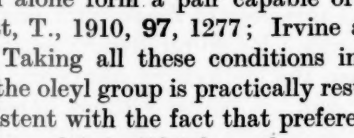
It seems advisable to withhold the description of these compounds meanwhile, as their production does not form part of the proof of the constitution of anhydro-methylglucoside mono-oleate, but is due to a side reaction of great complexity.

Further evidence as to the constitution of monomethyl anhydro-methylglucoside mono-oleate ($C_{26}H_{46}O_6$) was obtained by subjecting the compound to hydrolysis and examining the cleavage products. This was carried out in order to ascertain if the oleic acid was present as such or had undergone intramolecular change and also to identify the methylated glucoside produced.

Several methods of hydrolysis were attempted. The use of alkali gave, as the product from the oleyl portion of the molecule, a soap, the separation of which proved to be exceedingly difficult. Hydrolysis by means of aqueous acid was also unsatisfactory in that the original compound is an insoluble oil and one of the hydrolysis products is also insoluble in water. Under these conditions, hydrolysis is naturally slow and incomplete.

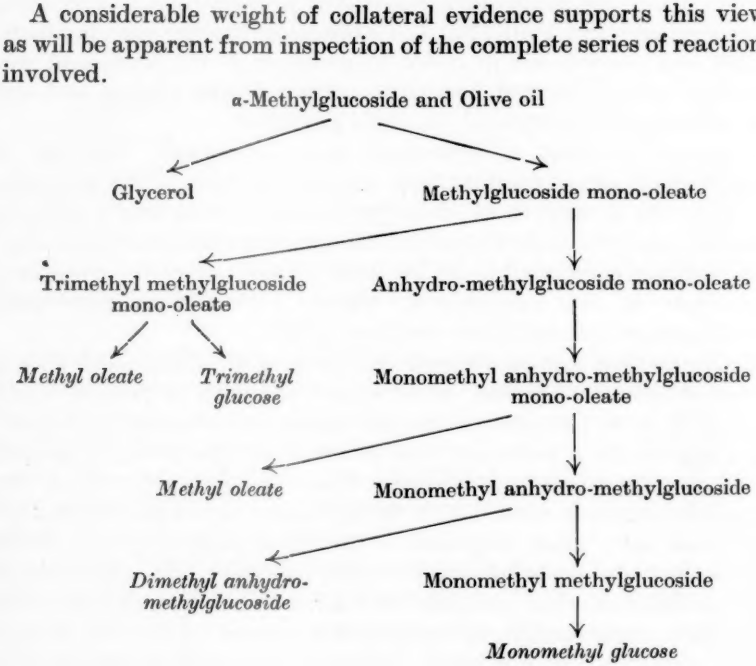
The method finally adopted was to heat the compound with a methyl-alcoholic solution of hydrogen chloride, a process which resulted in the formation of methyl oleate and *monomethyl anhydro-methylglucoside*. Attention was focussed on the latter compound and its reactions were studied. When treated with alkali, the anhydro-ring was opened with the formation of *monomethyl methyl-glucoside* and, when subjected to the silver oxide reaction, it was converted into *dimethyl anhydro-methylglucoside*. Two methylated glucosides were thus available for further constitutional study and, of these, monomethyl methylglucoside proved of greater service. The compound on hydrolysis yielded a monomethyl glucose and,

although this sugar failed to crystallise, it appeared to be a single compound. It reacted with phenylhydrazine, but gave no osazone under standard conditions, and the methyl group can thus be reasonably allocated to position 2. It follows that, in the original fat, the oleyl group must occupy one of the positions 3, 5, and 6. The two hydroxyl groups which are not esterified by oleic acid must satisfy the condition of being favourably situated to form an anhydride. This limits the choice, as the condition is best fulfilled by 5 and 6, which alone form a pair capable of giving a *cis*-ring (Irvine and Garrett, T., 1910, **97**, 1277; Irvine and Paterson, T., 1914, **105**, 898). Taking all these conditions into consideration, the attachment of the oleyl group is practically restricted to position 3, and this is consistent with the fact that preferential substitution in position 5 is unusual in artificial syntheses. The structure of methylglucoside fat may thus be represented by the formula



$(X = CO\cdot[CH_2]_7\cdot CH{:}CH\cdot[CH_2]_7\cdot CH_3)$

A considerable weight of collateral evidence supports this view, as will be apparent from inspection of the complete series of reactions involved.



EXPERIMENTAL.

Anhydro-methylglucoside Mono-oleate.

This preparation was carried out on many occasions and the following account is restricted to the conditions adopted in a typical case. Twenty-eight grams of α-methylglucoside (3 mols. and 3 grams excess) were mixed with 38 grams of olive oil (1 mol.) in the presence of 1·5 grams of sodium ethoxide, the proportions being adjusted so as to introduce one oleyl residue. The mixture was heated under diminished pressure until the temperature reached 220°, and, after cooling and acidification with acetic acid, the glycerol liberated in the reaction was removed by distillation in steam. The undistilled residue was extracted with ether, and the ethereal solution washed with water and dried over anhydrous magnesium sulphate. On evaporation of the solvent, the product remained as an extremely viscous, golden-yellow oil which proved to be anhydro-methylglucoside mono-oleate. The following analytical results, which were obtained with the product of different preparations, show the uniformity of the reaction [Found : C = 68·31, 68·15, 68·11; H = 10·08, 10·15, 10·37; OMe = 6·06, 6·10. Anhydro-methylglucoside mono-oleate ($C_{25}H_{44}O_6$) requires C = 68·18; H = 10·00; OMe = 7·04 per cent.].

All attempts to obtain the compound in a crystalline condition failed, and it also proved impossible, even in the high vacuum of the Gaede pump, to distil the material without decomposition.

The uniformity and purity of the compound, isolated as described, are, however, substantiated by the identity of the specific rotations of the products of different preparations.

No. of preparation.	Solvent.	*c.*	*l.*	[α].	$[\alpha]_D^{18°}$.
1	Ethyl acetate	1·2320	1	+0·41°	+33·29°
1	Chloroform	1·4128	1	0·54	38·22
2	Chloroform	2·3607	2	1·82	38·55
3	Chloroform	2·9307	1	1·12	38·21

Attempt to Prepare Anhydro-methylglucoside Dioleate.

A mixture of 18·5 grams of anhydro-methylglucoside mono-oleate (3 mols.) and 12·5 grams of olive oil (1 mol.) was heated in the presence of sodium ethoxide at 220° for three hours. The product was isolated and purified precisely in the manner described above. Analysis showed that unchanged olive oil had survived the reaction [Found : C = 70·08; H = 9·95. Anhydro-methylglucoside di-oleate ($C_{43}H_{76}O_7$) requires C = 73·30; H = 10·80. Olive oil ($C_{57}H_{104}O_6$) requires C = 77·38; H = 11·76 per cent.].

The idea that no second condensation takes place was confirmed

by heating a mixture of olive oil and methylglucoside in the proportions necessary to introduce two oleyl residues into the glucoside molecule. As in the previous instance, a mixture consisting of anhydro-methylglucoside mono-oleate and unchanged olive oil was obtained (Found : C = 70·26; H = 10·40). On heating this mixture with excess of methylglucoside and a trace of sodium ethoxide, the residual olive oil reacted to give anhydro-methylglucoside mono-oleate [Found : C = 68·31; H = 10·08. Anhydro-methylglucoside mono-oleate ($C_{25}H_{44}O_6$) requires C = 68·18; H = 10·00 per cent.].

Monomethyl Anhydro-methylglucoside Mono-oleate.

In this case also, only one typical experiment need be quoted, although the reaction was carried out on several occasions. 22·6 Grams of the mono-oleate (1 mol.) were dissolved in 58·4 grams of methyl iodide (4 mols.) and methylated in the usual manner by the addition of 47·8 grams of silver oxide (2 mols.). The reaction, which was spontaneous, was continued by warming on a water-bath under a reflux condenser for eight hours, an additional quantity of 20 grams of methyl iodide being added when the mixture became pasty. Ether was used as the extracting agent, the solution being dried over anhydrous magnesium sulphate and the solvent evaporated. Thereafter the oily residue was heated at 100°/10 mm. until constant in weight.

Analysis of the product, which was a clear yellow, mobile oil, gave for two independent preparations [Found : C = 68·90, 68·76; H = 10·58, 10·38; OMe = 14·96, 12·41. Monomethyl anhydro-methylglucoside mono-oleate ($C_{26}H_{46}O_6$) requires C = 68·72; H = 10·13; OMe = 13·66 per cent.].

Hydrolysis of Monomethyl Anhydro-methylglucoside Mono-oleate and Simultaneous Condensation of the Products with Methyl Alcohol.

The use of alkali as a means of removing the oleyl residue proved inconvenient and the yields were greatly diminished owing to the retention of the product in the soaps. On the other hand, acid hydrolysts removed the gluosidic methyl group in addition to the oleyl group. Resource was therefore had to the method of heating with methyl alcohol containing 0·5 per cent. of hydrogen chloride (Irvine and Rose, T., 1906, **89**, 814). 19·4 Grams of monomethyl anhydro-methylglucoside mono-oleate were dissolved in 600 c.c. of the acidified alcohol and boiled under a reflux condenser. The reaction, which was followed polarimetrically, was arrested after boiling the solution for 80 hours, the observed rotation decreasing from + 1·16° to + 0·94° and later increasing to + 1·20° ($l = 1$)

for $c = 3{\cdot}23$ per cent. The liquid was neutralised by means of barium carbonate, the barium chloride remaining in solution removed by agitation with lead carbonate, and the filtrate evaporated to dryness. The residue was shaken with ether in the cold and from the ethereal solution was isolated a faintly yellow oil which on distillation proved to be methyl oleate, b. p. 145—150°/0·10 mm.; n_D 1·4578 (Found : OMe = 10·91. Calc. for $C_{19}H_{36}O_2$, OMe = 10·47 per cent.). The ester was converted into the corresponding acid and the lead salt prepared [Found : Pb = 41·82. Calc. for $PbO,Pb(C_{17}H_{33}\cdot CO_2)_2$, Pb = 41·74 per cent.].

Monomethyl Anhydro-methylglucoside.

The syrup unextracted by cold ether was treated with boiling acetone. Evaporation of the solvent yielded an uncrystallisable syrup which was purified by extraction with ethyl acetate at the boiling point. The material extracted proved to be essentially monomethyl anhydro-methylglucoside [Found : C = 48·01; H = 7·54; OMe = 32·61. Monomethyl anhydro-methylglucoside ($C_8H_{14}O_5$) requires C = 50·52; H = 7·36; OMe = 32·63 per cent.]. Despite the close agreement of the methoxyl content, the syrup, which was acid in reaction, was obviously impure. In order to remove the acidity, the syrup was dissolved in water and heated with barium hydroxide, the product being isolated in the manner already described as a clear, colourless, viscous, neutral syrup. Analysis now showed that under these conditions, not only had the acid been destroyed, but the anhydro-ring had opened out to give the normal glucoside [Found : C = 46·26; H = 7·65. Monomethyl methylglucoside ($C_9H_{16}O_6$) requires C = 46·15; H = 7·69 per cent.].

Dimethyl Anhydro-methylglucoside.

2·6 Grams of monomethyl anhydro-methylglucoside (1 mol.) were dissolved in 7·8 grams of methyl iodide (4 mols.) and methylated in the usual manner by the addition of 6·4 grams of silver oxide (2 mols.), a small quantity of methyl alcohol being added to aid solution. The product was extracted with boiling absolute alcohol and, after evaporation of the solvent and subsequent drying of the residue under diminished pressure, was obtained as a clear syrup now soluble in methyl iodide. A further methylation was carried out, in the absence of an extraneous solvent, the quantities of the reagents used being identical with those mentioned above. Heating was continued for eight hours, and the product was then extracted three times with boiling ether.

The syrup ultimately isolated was fairly mobile and boiled at

115—120°/0·20 mm. (n_D 1·4419) [Found : OMe = 44·55. Dimethyl anhydro-methylglucoside ($C_9H_{16}O_5$) requires OMe = 45·58 per cent.].

Hydrolysis of Monomethyl Methylglucoside.

As no crystallising medium was found for monomethyl methylglucoside, the compound was hydrolysed to give monomethyl glucose, which, it was hoped, would be a solid sugar. The hydrolytic agent employed was a 5 per cent. solution of hydrogen chloride, and the reaction was conducted at the temperature of boiling water. The rotation gradually diminished from $\alpha = +4{\cdot}68°$ to $+2{\cdot}95°$ for $c = 5{\cdot}00$ ($l = 1$) in the course of 150 minutes. At this stage, the sugar was isolated in the usual manner, but the compound proved to be an uncrystallisable syrup and was not further examined, beyond confirming its composition and ascertaining its behaviour towards phenylhydrazine.

The foregoing research was conducted under the auspices of the Food Investigation Board. Acknowledgment is due to the Board for providing the facilities required and for permission to publish the results.

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UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,
UNIVERSITY OF ST. ANDREWS. [*Received, November 7th*, 1923.]

II.—*The Condensation of Mannitol with Olive Oil.*

By JAMES COLQUHOUN IRVINE and HELEN SIMPSON GILCHRIST.

THE results described in the preceding paper have been applied to the investigation of the "mannitol fat" prepared by the interaction of mannitol and olive oil in the presence of sodium ethoxide (Lapworth and Pearson, *Biochem. J.*, 1919, **13**, 296). On the evidence of analysis, this synthetic fat contains mannitan dioleate and *iso*mannide dioleate, but the exact composition of the mixture and the structure of the constituents remained uncertain.

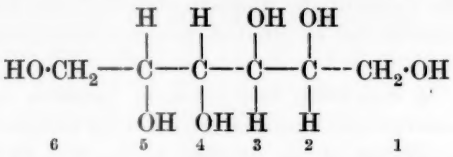
It will be recalled that in the preparation of a "methylglucoside fat" by parallel methods, the first compound formed is methylglucoside mono-oleate which, on heating at 200°/10 mm., loses a molecule of water and is converted into anhydro-methylglucoside mono-oleate. This behaviour suggests that the analytical samples of mannitol fat, in the condition in which they were used, did not represent precisely the composition of the original material. The specimens were dried for several hours at 200—220° under diminished

pressure before being submitted to analysis and, in our experience, this treatment results in molecular dehydration. It would therefore appear that the *iso*mannide dioleate detected by Lapworth and Pearson in mannitol fat originated principally during the drying process.

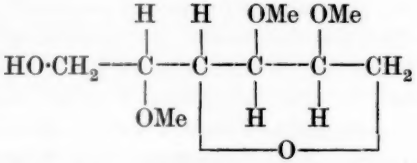
Accordingly, in repeating the reaction between mannitol and olive oil, we removed the liberated glycerol by distillation in steam and limited the drying of the product to heating at 100°/10 mm. Under these conditions, the essential compound formed is mannitan dioleate contaminated with a trace of *iso*mannide, together with a small quantity of mannitol, which lowered the carbon and hydrogen values; no *iso*mannide dioleate was present. The persistence with which unchanged mannitol remains dissolved in the synthetic fat is remarkable, as this impurity resists the effect of boiling water and is not removed even by washing a dilute ethereal solution. Examination of the products of numerous preparations leads to the opinion that the first reaction in the condensation of mannitol with olive oil is the formation of mannitol dioleate. This, in turn, is readily dehydrated to give mannitan dioleate and, under more drastic conditions, a second molecule of water is lost and *iso*mannide dioleate is produced. Simultaneously, any free mannitol left dissolved in the fat is ultimately converted into *iso*mannide. There is no sharp line of demarcation between these consecutive reactions, although, under conditions described in the experimental part, a mannitol fat can be obtained which contains 90 per cent. of mannitan dioleate. Information bearing on the constitution of this compound was obtained by subjecting the fat to methylation, a process which yielded monomethyl mannitan dioleate together with a trace of monomethyl *iso*mannide. The latter was removed by distillation and the residual methylated fat was thereafter decomposed to give ethyl oleate and monomethyl mannitan. This, in turn, was converted into trimethyl mannitan and, as the alkylation remained completely suspended at this stage, it was evident that one of the terminal hydroxyl groups of the hexitol chain remained intact (Irvine and Paterson, T., 1914, **105**, 915).

Obviously the structure of the original mannitol fat can be deduced if the constitution of the above trimethyl mannitan is known. Preserving the condition that a terminal hydroxyl group is unsubstituted, the compound may be formulated in ten different ways, and although our experiments do not serve to discriminate between these possibilities, the combined results of the research lead to a consistent structural formula for mannitan dioleate. In the original condensation, the ease of formation of the anhydro-ring points to the fact that, after the oleyl residues had entered the hexitol chain,

the usual positions for anhydro-ring formation were still unsubstituted. If the stereochemical formula for mannitol be written as

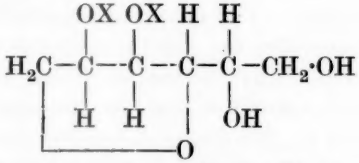


it is evident that the anhydro-ring may couple any two of the hydroxyl groups with the exception of 6. Previous researches on mannitol have shown that these groups display a tendency to form five-membered rings possessing a *cis*-linking (Irvine and Paterson, T., 1914, **105**, 898). The above conditions are satisfied only if the oxygen atom of the ring connects positions 1 and 4, so that the most probable formula for trimethyl mannitan is



On this basis, the oleyl residues in the mannitol fat must occupy two of the three positions 2, 3, and 5, but as substitution in position 5 of the mannitol chain is difficult the location of the acyl residues is practically restricted to 2 and 3.

Taking all these factors into consideration, and so far as the present experimental evidence leads, the formula for " mannitol fat " may be stated as



$(X = CO\cdot[CH_2]_7\cdot CH{:}CH\cdot[CH_2]_7\cdot CH_3)$

Experimental.

Mannitan Dioleate.

The preparation of a mixture of mannitan and *iso*mannide dioleates has been described by Lapworth and Pearson (*loc. cit.*). As under the conditions outlined there is no guarantee that all the glycerol has been removed from the system, a further purification was considered necessary, and the synthetic fat, after having been acidified with acetic acid, was subjected to distillation in steam.

The undistilled residue was dissolved in ether, washed repeatedly with water, and the solution dried over magnesium sulphate. On distilling the solvent, at first under ordinary pressure and later under diminished pressure, the product was obtained as a pale yellow, very viscous oil, which became practically solid at the ordinary temperature. Analysis showed that the main constituent of the fat was mannitan dioleate, but as the figures obtained were not in complete agreement with the calculated values, some impurity was evidently present [Found : C = 70·03, 69·93; H = 10·32, 10·44. Mannitan dioleate ($C_{42}H_{76}O_7$) requires C = 72·83; H = 10·98 per cent.]. The low value obtained for both carbon and hydrogen led to the conclusion that the impurity was mannitol or one of its dehydration products. As mannitol ($C_6H_{14}O_6$) requires C = 39·56; H = 7·69 per cent., it is evident that a small percentage of this compound would seriously affect the combustion values of the synthetic fat. Moreover, it was found that mannitol is soluble in mannitan dioleate on heating, and does not separate out on cooling the solution.

Monomethyl Mannitan Dioleate.

The quantities of reagents employed were calculated on the assumption that in mannitan dioleate two hydroxyl groups of the molecule are free for methylation. Thirty grams of mannitan dioleate (1 mol.) were dissolved in 49·3 grams of methyl iodide (8 mols.) and methylated by the addition of 40·2 grams of silver oxide (4 mols.). The reaction, which was spontaneous, proceeded normally and was completed by heating for eight hours on a water-bath. The methylated product, isolated in the usual manner, proved to be essentially monomethyl mannitan dioleate [Found : OMe = 6·1. Monomethyl mannitan dioleate ($C_{43}H_{78}O_7$) requires OMe = 4·5 per cent.]. As only one methyl group had entered the chain, it was deemed advisable to carry out a futher methylation to ascertain if the remaining free hydroxyl group could be substituted. It was found, however, that no increase took place in the methoxyl content (Found : OMe = 5·9 per cent.). This result adds another example to the cases of steric hindrance encountered in the mannitol series.

It will be seen that the value of the methoxyl content is slightly high, which is consistent with the idea that a small proportion of mannitol had escaped condensation and had subsequently undergone methylation. The methylated fat was accordingly heated at 200°/10 mm. and as the temperature rose from 100° to 160°, a few drops of a volatile compound distilled (n_D 1·4506). Estimation of the methoxyl content of this distillate gave the notably high value of

(1) 20·67; (2) 18·10. Monomethyl *iso*mannide ($C_7H_{12}O_4$) requires OMe = 19·38 per cent. Although it was difficult to carry out accurate analysis on such a small scale, it is quite evident that the original fat contains some impurity, in all probability a dehydration derivative of mannitol, which on methylation gives a compound having a much greater methoxyl content then the normal product. This accounts adequately for the analytical result previously reported for monomethyl mannitan dioleate.

Hydrolysis of Monomethyl Mannitan Dioleate and Simultaneous Condensation of the Acid Product with Ethyl Alcohol.

A 4 per cent. solution of the methylated mannitol fat in ethyl alcohol containing 0·5 per cent. of hydrogen chloride was heated according to the method adopted by Irvine and Rose (T., 1906, **89**, 814). A small quantity of charcoal was added to the solution, which was boiled under a reflux condenser for eighty hours. The liquid was then neutralised with barium carbonate, the filtrate being evaporated to dryness under diminished pressure, after which the residue was extracted with absolute alcohol, the solution filtered, and the solvent distilled. On extracting the product with cold ether and evaporation of the solvent, a colourless, highly refractive liquid remained (b. p. 125—130°/0·02 mm., n_D 1·4544) [Found : OEt = 15·35. Ethyl oleate ($C_{20}H_{38}O_2$) requires OEt = 14·52 per cent.].

Monomethyl Mannitan.

The material left unextracted with cold ether in the above preparation was dissolved in acetone containing a little alcohol and gave, on subsequent evaporation of the solvents, a very viscous syrup. This was purified by extraction with ethyl acetate at the boiling point, and proved to be monomethyl mannitan [Found : C = 46·98; H = 8·00; OMe = 15·74. Monomethyl mannitan ($C_7H_{14}O_5$) requires C = 47·19; H = 7·92; OMe = 17·41 per cent.].

Trimethyl Mannitan.

Monomethyl mannitan, obtained as above, was subjected to the silver oxide reaction. The reaction mixture consisted of 1·5 grams of monomethyl mannitan (1 mol. containing three free hydroxyl groups), 11·7 grams of silver oxide (6 mols.), and 14·4 grams of methyl iodide (12 mols.), a little methyl alcohol being added to aid solution. The product on isolation was subjected to a second methylation, in which no extraneous solvent was required, as the partly methylated syrup was freely soluble in methyl iodide. This second reaction yielded a clear syrup (n_D 1·4528) and after a third treatment the refractive index was unaltered, showing that

no further methylation had taken place. On distillation under diminished pressure (b. p. 115—120°/0·18 mm.), the product was isolated as a clear, mobile syrup (n_D 1·4518). Analysis showed that the terminal hydroxyl group in the chain had resisted methylation, thereby proving that the anhydro-linking in the original fat must occur between two other groups of the alcohol chain [Found : C = 52·72; H = 8·56. Trimethyl mannitan ($C_9H_{18}O_5$) requires C = 52·42; H = 8·73 per cent.].

The thanks of the authors are due to the Food Investigation Board, under whose auspices the work was conducted.

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III.—*The Constitution of Polysaccharides. Part VII. Esparto Cellulose.*

By JAMES COLQUHOUN IRVINE and EDMUND LANGLEY HIRST.

IT is now recognised that the expression "cellulose" is applied in a general sense and is made to include a number of closely-related substances which, whilst they display many physical and chemical features in common, are so divergent in their properties that they must be regarded as different chemical individuals. This point has not been overlooked in our investigations on molecular structure and accordingly our earlier work in this field was carried out on cotton cellulose, which is regarded as the standard example of a normal cellulose. The cellulosic constituents of many other fibre-bearing plants show variations from this standard and the question is raised as to whether such substances are mixtures, containing cotton cellulose as one constituent, or are composed essentially of an isomeric variety of the polysaccharide. This does not exhaust the alternatives and, theoretically, it is possible that polysaccharides of many different types may exist. For example, these compounds may in some cases consist of large molecules or they may be polymerides of simple molecules containing identical or different hexose units. Finally, they may consist of polymerised units in which hexose residues are condensed with either higher or lower members of the sugar group. It is evident that even the elementary study of different varieties of cellulose is complicated if consideration is given to all the theoretical possibilities involved.

We have selected esparto cellulose for inclusion in our research programme, partly in view of its technical importance but principally on account of its comparative simplicity and close relationship to cotton cellulose. As is well known, approximately one-half of the weight of dried esparto grass can be extracted on boiling with sodium hydroxide (preferably under pressure) and the residue constitutes an important paper-making material. Esparto cellulose is not, however, identical with cotton cellulose. The distinction is more than physical as, apart from variations in property which are attributable to the condition of the fibres and are thus apparent in mechanical working, this variety of cellulose is characterised by a number of special reactions. Amongst these is the formation of furfural on heating with acids, a result which indicates the presence of a pentose constituent. Prolonged digestion with sodium hydroxide gradually eliminates this component, and the extract is found to contain a " pentosan " which may be precipitated. It follows, in consequence, that the esparto cellulose of the paper-maker will always contain a variable amount of one component capable of yielding furfural and the proportion of this constituent will depend on the conditions adopted in the preliminary treatment with alkali. In general, about 80 per cent. of esparto cellulose is composed of authentic cellulose possessing the formula $(C_6H_{10}O_5)_x$, and convertible quantitatively into a hexose on hydrolysis.

Taking these factors into consideration, esparto cellulose may consist of (1) a mixture of polysaccharides derived respectively from hexose and pentose units, or (2) a mixed polysaccharide in which the hexose and pentose residues are condensed together. It was with the object of discriminating between these alternatives and of definitely identifying the parent hexose and pentose sugars that the present research was undertaken.

The process of disrupting a cellulose by the action of highly concentrated acid offers little prospect of success in this particular case, as the liberation of furfural introduces serious complications. This method of attack has already been explored by Cunningham (T., 1918, **113**, 173) and in the course of a separate investigation (Hirst and Robertson, forthcoming paper) the limitations attached to the process have been defined. We have accordingly utilised the series of reactions originally designed to ascertain the composition of cotton cellulose and have converted esparto cellulose into the fully substituted acetate (in this case a mixture), from which the corresponding methylhexoside and methylpentoside were prepared.

The esparto cellulose employed was obtained from Spanish

Grass, which was subjected to the usual boil with alkali and the residue thereafter treated with moist chlorine to remove colouring matter and residual lignin. Although the white, fibrous mass was apparently uniform, it yielded 12 per cent. of its weight of furfural on distillation with acid; the result corresponds to the presence of 18·5 per cent. of a pentosan, and this constituent was completely removed by prolonged extraction with boiling sodium hydroxide solution. The materials requiring separate examination were thus:

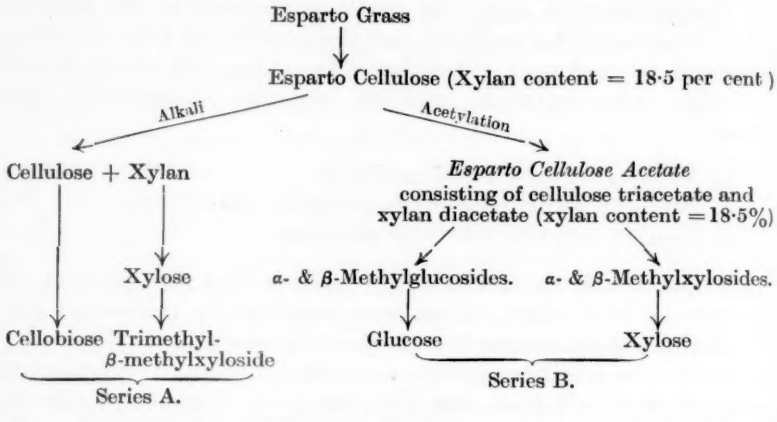
(*a*) Esparto cellulose free from lignin.
(*b*) Pentosan constituent extracted from (*a*).
(*c*) Esparto cellulose free from pentosan.

Description will be facilitated by stating that the product (*b*) proved to be a *xylan*, which was identified by conversion into crystalline xylose and also into the characteristic trimethyl β-methyl xyloside. In addition, product (*c*) was transformed by standard methods into cellobiose and also into 2 : 3 : 6-trimethyl glucose, so that, in essential chemical character, this constituent is molecularly akin to, if not actually identical with, the cellulose of cotton. Special attention was therefore directed to esparto cellulose in the original form in which the xylosan component is still present.

On acetylation, the cellulose yielded a fully substituted acetate and as the loss of pentosan in this reaction was negligible the product contained both a hexosan triacetate and a pentosan diacetate. On the basis of analysis, the total yield of acetate was 97·2 per cent. of the theoretical amount, a result which may be taken as quantitative in view of the experimental difficulties involved. Thereafter, by heating with methyl alcohol containing hydrogen chloride, the esparto cellulose acetate was converted into a crystalline mixture of methylglucoside and methylxyloside. This modification of the usual method of hydrolysing a carbohydrate complex proved of material service in preserving the quantitative aspect of the work, as the xylose on liberation was continuously transformed into methylxyloside and was thus protected from the destructive action of the hydrochloric acid. By means of control experiments, conducted with artificial mixtures of glucose and xylose, conditions were established which diminished the loss of pentose in the reaction to a minimum (3 per cent.). The joint weight of methylglucoside and methylxyloside thus obtained corresponded to 91·9 per cent. of the theoretical quantity and a sample of the total product, when hydrolysed with dilute aqueous acid, gave a mixture of glucose (84 per cent.) and xylose (16 per cent.).

Discussion of Results.

To facilitate reference the complete series of transformations involved in the research may be represented by the scheme :—



Series A has no quantitative significance, but furnishes evidence as to the constitution of the two main components. On the other hand, series B represents a sequence of quantitative operations and the over-all yields of pure crystalline products show that, as a minimum, the esparto cellulose employed was converted to the extent of 89·4 per cent. into glucose and xylose. The experimental loss is almost entirely due to the formation of traces of furfural and, as this factor was controlled at each stage by analysis, it is possible to recalculate the results. On introducing the necessary correction, the combined glucose and xylose obtainable from esparto cellulose is 92·0 per cent. of the amount theoretically possible according to the equation

$$n(C_6H_{10}O_5)_x m(C_5H_8O_4)_y \longrightarrow xnC_6H_{12}O_6 + ymC_5H_{10}O_5.$$

In the particular samples of esparto cellulose employed, the ratio $nx : my$ was 4·04 : 1, but, although typical, this is a variable and is entirely dependent on the conditions of the preliminary boiling process. A sample of esparto cellulose may in fact contain any proportion of xylan from about 20 per cent. downwards. Unless the unlikely assumption is made that the action of alkali is preferential and, whilst leaving hexose units largely unattacked, detaches and dissolves combined pentose units from a polysaccharide, it follows that esparto cellulose is not a chemical individual but is a mixture. This was supported by the fact that when esparto cellulose was subjected to acetolysis under varied conditions no trace of any disaccharide containing a xylose residue was detected.

On the other hand, cellobiose was obtained by the acetolysis of the hexose cellulose which remained after complete removal of the xylose cellulose by the action of alkali.

Inspection of the experimental details gives an indication of the relative molecular complexity of the two components present in esparto cellulose. The ready solution of the xylan constituent in alkali and the fact that after precipitation it may be dissolved in hot water point to a comparatively low molecular weight. On the other hand, the extreme resistance to attack by reagents displayed by the hexose cellulose is even more pronounced than in the case of cotton. Up to the present, our experiments do not serve to show if the xylan is mechanically mixed with the hexose cellulose or if the two constituents form a solid solution. Microscopic examination of esparto fibre and of the acetates to which it gives rise supports the latter view and this aspect of the general inquiry is being included in an extension of the research.

Summary.

1. Esparto cellulose in the condition in which the material is used for paper-making is a mixture (or more probably a solid solution) of a genuine hexose cellulose (81·5 per cent.) and a pentosan (18·5 per cent.).

2. The hexose cellulose is composed entirely of glucose residues, is convertible into cellobiose and also into 2 : 3 : 6-trimethyl glucose In these respects, and also in its high molecular complexity, the compound resembles the cellulose of cotton.

3. The pentosan component is a polymerised anhydro-xylose and may be isolated as a definite xylan which yields xylose on hydrolysis.

4. Esparto cellulose yields on acetylation the triacetate of the glucose cellulose together with the diacetate of the xylan. Yield 97·2 per cent.

5. The product of acetylation has been converted into mixtures of α- and β-methylglucoside with α- and β-methylxyloside. Yield 91·9 per cent.

6. No sugars other than glucose and xylose have been detected in the hydrolysis products obtained from esparto cellulose.

7. A method of preparing xylose from esparto cellulose is described.

Experimental.

The "boiled esparto grass" used in the present investigation was supplied by Messrs. Tullis Russell & Co., of Markinch. It had been subjected to the usual extraction with 6 per cent. aqueous alkali under 45 lb. steam pressure, but was still unbleached and showed in places portions of unchanged lignin. With the object of

obtaining a starting material which would be as far as possible a normal esparto cellulose, the colouring matter and the residual lignins were removed by treatment with moist chlorine. After thorough washing with warm water and drying in air, the esparto cellulose presented the appearance of a white, fibrous mass containing moisture 10·5 and ash 1·07 per cent. Distillation with 12 per cent. aqueous hydrochloric acid gave an amount of furfural, estimated as the phloroglucide compound (Krüger and Tollens, *Z. angew. Chem.*, 1896, **2**, 33), corresponding to 18·5 per cent. of xylan (Kröber, *J. Landw.*, 1900, **48**, 379). In view of the later experiments, which indicated the absence of other pentoses, the figures quoted refer to pentosans in the form of xylan.

Acetylation of Esparto Cellulose.

Acetylation of esparto cellulose by Barnett's method did not proceed so readily as in the case of cotton cellulose (Irvine and Hirst, T., 1922, **121**, 1585), but the difficulties appeared to be chiefly mechanical and to be due to the failure of the acetylating reagents to penetrate the hard, compact surface of the dry material. In preliminary experiments, efforts were made to disintegrate the esparto cellulose by rapid mechanical agitation in boiling water, but these proved to be unsuccessful owing to the very extensive "ricing" which took place. Acetylation could be accelerated by raising the temperature of the reaction, but this promoted the destruction of the pentose constituent. The most satisfactory results were obtained by the method now described, by means of which more than 200 grams of esparto cellulose acetate were prepared. Fourteen grams of air-dried, finely-shredded esparto cellulose were incorporated with 60 c.c. of glacial acetic acid, through which a stream of dry chlorine had been passed for thirty seconds, and 60 c.c. of acetic anhydride were thereafter added. After efficient stirring of the mixture, sulphur dioxide gas was bubbled through the mass for one minute and the whole then continuously stirred for a period of several hours. The spontaneous rise of temperature was small and, after two hours, the esparto cellulose gelatinised and dissolved slowly. The later stages were hastened by warming the mixture at 40°, and at the end of twenty-four hours a clear, almost colourless solution was obtained which was treated with chloroform and water in the manner already described for cotton cellulose acetate (Irvine and Hirst, *loc. cit.*). The acetate when dried at 100° weighed 21·06 grams. Calculating for the triacetate of a $C_6H_{10}O_5$ unit and a diacetate of a $C_5H_8O_4$ unit, present in the proportions of 82 per cent. and 18 per cent., respectively, and allowing for the moisture and ash content, this

yield corresponds to 97·2 per cent. of the theoretical value. The aqueous portion gave a slight trace of reduction with Fehling's solution and consequently the whole of the filtrate and the washings were distilled in steam to remove acetic acid, boiled with 4 per cent. hydrochloric acid for nine hours to hydrolyse any acetate, and thereafter evaporated to a small bulk. This solution showed no optical activity; the residue left after neutralisation and evaporation to dryness had practically no action on Fehling's solution, thus proving that the weight of water-soluble material formed during acetylation was negligible.

Esparto Cellulose Acetate.—The esparto cellulose acetate was white in colour and differed from cotton cellulose acetate, prepared in the same manner, by being softer in texture and more sensitive to high temperatures. Decomposition of the majority of specimens began at 120°, but this was variable and appeared to depend largely on the efficiency of the washing process in eliminating every trace of acid. The acetate was soluble in chloroform and acetone, but insoluble in alcohol. The specific rotation of a chloroform solution was of the order $-20°$ ($c = 1·2$), but, owing to the cloudiness of the solution, this value is only approximate [Found: Moisture = 1·5; ash = 0·29; C = 49·8; H = 5·46; $CH_3{\cdot}CO$ = 44·9; furfural = 6·9. Calc. (for a mixture containing 18·5 per cent. of xylan before acetylation), C = 50·0; H = 5·55; $CH_3{\cdot}CO$ = 43·6; furfural = 6·8 per cent.]. No loss of pentosan had therefore occurred during the acetylation.

Conversion of Esparto Cellulose Acetate into Methylglucoside and Methylxyloside.

As in the case of cotton cellulose acetate, it was found that on treatment at 120—130° with methyl alcohol containing a small proportion of hydrogen chloride, esparto cellulose acetate gradually dissolved with elimination of the acetyl groups, together with hydrolysis of the polysaccharide and condensation of the products of hydrolysis with methyl alcohol. Under parallel experimental conditions, it was invariably the case that esparto cellulose acetate was more resistant to the action of these reagents than cotton cellulose acetate. On account of this difficulty, higher temperatures and longer periods of treatment were required, and this involved slight loss of material owing to traces of decomposition. Careful temperature control was thus required and, even under the best experimental conditions, partial destruction of the pentose residues took place. Control experiments on the action of acid methyl alcohol on xylose at 120—130° proved that the decomposition of the pentose with formation of furfural was unavoidable. The

yields quoted below, which have been confirmed on several occasions, must therefore be taken only as minima. It was found convenient to use 4 grams of esparto acetate in each experiment, the material being heated with 60 c.c. of methyl alcohol containing 1·5 per cent. of hydrogen chloride at 130° for 120 hours. The solid remaining undissolved weighed 0·12 gram and consisted partly of ash (silica) and partly of regenerated cellulose. After one treatment with animal charcoal, the solution was only slightly coloured, and by the usual procedure gave 2·490 grams of syrup, precautions being taken to ensure the complete dryness of the product. The calculated quantity of mixed glucoside and xyloside obtainable from 4 grams of an acetate giving 6·9 per cent. of furfural is 2·710 grams, and the yield was therefore 91·9 per cent. of the theoretical amount. The syrup crystallised spontaneously (m. p. 105—150°; $[\alpha]_D$ +90·0° for $c = 1{\cdot}200$ in acid methyl alcohol). This optical value was permanent, no change being recorded after further treatment in a sealed tube at 100°. Analysis of the crystalline product showed that a loss of 3 per cent. of pentose had occurred, and this corresponds to approximately 16 per cent. of the total pentose present [Found: C = 43·3; H = 7·25; OMe = 15·6; xylose = 15·7. Calc., for a mixture of $C_6H_{14}O_7$ (84 per cent.) and $C_5H_{12}O_6$ (16 per cent.), C = 43·4; H = 7·23; OMe = 16·4 per cent.].

On recrystallisation from ethyl alcohol, pure α-methylglucoside was obtained (m. p. 164°) and a polarimetric study of the hydrolysis of the mixed hexoside and pentoside from the sealed tubes showed that the material consisted of α- and β-methylglucosides together with α- and β-methylxylosides. 0·4140 Gram dissolved in 25 c.c. of 3 per cent. aqueous hydrochloric acid and heated at 100° with the addition of a small quantity of charcoal, gave the following readings ($c = 1{\cdot}656$):

Time	0 min.	45 mins.	90 mins.	240 mins.
$[\alpha]_D$	+90°	59·1°	46·2° *	45·6° * (constant)

* Concentration calculated on weight of sugar formed during hydrolysis.

The equilibrium value of the specific rotation of a mixture of glucose (84 per cent.) and xylose (16 per cent.) is + 46·6°. Further evidence was obtained by estimation of the sugar present after hydrolysis by Allihn's method. Ten c.c. of the solution after completion of hydrolysis gave (after neutralisation) on treatment with Fehling's solution 288·8 mg. of copper (calculated 294 mg.).

Behaviour of Artificial Mixtures of Xylose and Glucose.

The identification of the pentose constituent as xylose was confirmed by comparing the behaviour of an artificial mixture

of glucose (84 per cent.) and xylose (16 per cent.) with that of the material isolated from the sealed-tube experiments. 5·0 Grams of such a mixture were treated with acid methyl alcohol at 100° for twenty-four hours, and the mixture of methylxylosides and methylglucosides was isolated in the usual manner. Yield 5·3 grams, or 97·5 per cent. of the theoretical amount. This mixture crystallised spontaneously (m. p. 105—140°) and showed $[\alpha]_D$ +90·6° in acid methyl alcohol for $c = 1·445$ (Found: C = 43·3; H = 7·07; OMe = 16·1; xylose = 15·4. Calc., C = 43·25; H = 7·24; OMe = 16·4; xylose = 16·0 per cent.). On hydrolysis, under the same conditions as before, 0·527 gram, dissolved in 25 c.c. of 3·5 per cent. aqueous hydrochloric acid, gave the following figures on heating at 100° ($c = 2·108$):

Time	0 min.	45 mins.	180 mins.	270 mins.	300 mins.
$[\alpha]_D$	+90°	58°	48·6°	46·1° *	46·1° *

* Concentration recalculated on weight of free sugar formed.

The calculated value for the end-point is + 46·6°. When treated with Fehling's solution, 3·2 c.c. of the fully hydrolysed solution gave 123 mg. of copper (calc. 121 mg.).

Control Experiments.

The above evidence as to the identity of the pentose constituent is based on polarimetric readings and is valid only if xylose is stable under the conditions of hydrolysis. In view of the marked action of dilute mineral acids on pentoses, it was necessary to study the action of 3 per cent. aqueous hydrochloric acid on xylose. With exactly the same experimental conditions as those described above, the following observations were recorded which prove the stability of xylose in so far as the present series of experiments is concerned.

Time	0 min.	90 mins.	240 mins.
$[\alpha]_D$	+20·6°	20·2°	19·2°
Unchanged xylose per cent.	100	99	92

Slight traces of furfural were observed after 150 minutes. The amount of xylose remaining after 250 minutes was confirmed (after steam distillation to remove any furfural) by a copper estimation.

Reactions of Esparto Cellulose free from Xylan.

As stated in the introduction, esparto cellulose which has been extracted with alkali until all xylan has been removed displays the essential chemical properties of cotton cellulose. The conversion into cellobiose octa-acetate was carried out with small quantities

of material in order to secure efficient temperature control, and the following is an account of a typical experiment.

Two grams of extracted esparto cellulose were treated at 15° with a mixture of 30 c.c. of acetic anhydride and 3 c.c. of concentrated sulphuric acid. The temperature was then suddenly raised to 110° and maintained at this point until the solution became nearly black. On pouring into excess of cold water, cellobiose octa-acetate was precipitated, and this, after washing with water and recrystallisation from ethyl alcohol, weighed 0·35 gram. Under exactly parallel conditions, control experiments with 2-gram lots of cotton cellulose gave 0·38 gram of the octa-acetate.

Similarly, when exhausted esparto cellulose was methylated by methyl sulphate and alkali, alkylation proceeded as in the case of cotton cellulose and a trimethyl derivative was formed. This was converted by standard processes into the corresponding trimethyl methylglucoside, which was finally hydrolysed to give the parent substituted glucose. As a result of these operations, 2 : 3 : 6-trimethyl glucose was obtained displaying the physical constants characteristic of this compound.

These reactions point to the chemical identity of cotton cellulose with extracted esparto cellulose, but it is worthy of mention that in no case was cellobiose octa-acetate obtained from material which had not been fully exhausted with alkali.

Preparation of Xylose from Esparto Cellulose.

This was accomplished in two stages, in the first of which xylan was isolated and this was afterwards hydrolysed to give crystalline xylose.

One hundred parts of esparto cellulose were boiled gently, with frequent stirring, for ten to twelve hours with a solution of 120 parts of sodium hydroxide in 1,000 parts of water. The residual solid was filtered (using a porcelain Buchner funnel without filter-paper) and well pressed. This residue still contained about 1·8 per cent. of pentosan, which was removed completely by a second treatment with the alkali. On cooling the dark brown filtrate to 50° and adding an equal bulk of 90 per cent. alcohol, a white, flocculent precipitate formed and, after standing for twelve hours, the supernatant liquid was poured away. The crude xylan was then filtered rapidly and, while still moist, was triturated with aqueous acetic acid to remove alkali, after which the material was washed with water, alcohol, and ether in succession. Unless the xylan was dried slowly and at a low temperature the material became discoloured and formed a hard, horny mass. Yield 15—16 parts. In this condition, the xylan contained 3—4 per cent. of

mineral matter and gave a yield of furfural corresponding with a xylan content of 91 per cent.

Hydrolysis was effected by dissolving in 2 per cent. aqueous sulphuric acid and heating at 90°, when the rotation altered to dextrorotatory and remained constant after six to eight hours' treatment. Judging from the optical value, the amount of xylose then present was about 75 per cent. of the theoretical weight, the loss being due to the formation of furfural. After neutralisation with barium hydroxide, the filtered solution was evaporated under diminished pressure, when the syrup thus obtained crystallised spontaneously. The average yield was of the order 35—40 per cent. of the theoretical amount, but occasionally yields of more than 50 per cent. were obtained. No pentoses other than xylose were detected in any of the experiments and this was confirmed by preparing the characteristic xylose phenylosazone from (*a*) the recrystallised sugar, (*b*) the original crude syrup, and (*c*) the mother-liquors accumulated during recrystallisations. In each case the osazones were identical under the microscope and melted at 152—160° with decomposition. The recrystallised xylose showed the correct mutarotation and permanent specific rotation ($[\alpha]_D^{20°}$ + 19°) and melted at 143—144°. The figures quoted in the literature vary from 140° to 145°, and a mixed melting point with an authentic specimen showed no depression.

Final confirmation of the identity of the pentose was obtained by the methylation process, which gave the same trimethyl β-methyl-xyloside as had previously been obtained from xylose (Carruthers and Hirst, T., 1922, **121**, 2299).

The investigation of the subjects dealt with in the present paper is being continued, and we desire to reserve the application, to cellulose, of methods developed in this laboratory. We also take the opportunity to express our thanks to Messrs. Tullis Russell and Co., for valuable help in the provision of material, and to the Carnegie Trust for a Fellowship which enabled one of us to take part in the work.

Chemical Research Laboratory,
United College of St. Salvator and St. Leonard,
University of St. Andrews. [*Received, November 6th*, 1923.]

IV.—*Camphorylcarbamates and their Physiological Action.*

By Hans Eduard Fierz-David and Walter Müller.

Forster and Fierz (T., 1905, **87**, 110) prepared methyl and ethyl camphorylcarbamates by the interaction of camphorylcarbimide with the corresponding alcohols, but the method and also the yields were unsatisfactory. A very simple method of preparation consists in the interaction of aminocamphor and alkyl chloroformates, the urethanes being obtained in almost quantitative yield:

$$C_8H_{14}\begin{cases}CH\cdot NH_2\\ |\\ CO\end{cases} + CO\begin{cases}Cl\\ OAlk\end{cases} = C_8H_{14}\begin{cases}CH\cdot NH\cdot CO\cdot OAlk\\ |\\ CO\end{cases} + HCl.$$

Thirty-seven grams of *iso*nitrosocamphor, dissolved in 150 c.c. of 30 per cent. sodium hydroxide, were reduced with 37—40 grams of zinc dust, the base was removed with ether and extracted therefrom with 40 per cent. hydrochloric acid. The aqueous solution was twice extracted with 50 c.c. of ether and the dissolved ether removed by a current of air at 80°. The solution of aminocamphor hydrochloride, mixed with 100 c.c. of 30 per cent. sodium hydroxide, was heated at 60° and stirred mechanically while the chloroformic ester (110 per cent. of the theoretical quantity) was added slowly. The urethane, which separated as a viscous mass, was distilled under diminished pressure. iso*Amyl* and *allyl camphorylcarbamates* are viscous, oily liquids; the others mentioned in the table crystallise in long, lustrous needles.

Camphorylcarbamate.	M. p.	B. p.	$[\alpha]_D$ in $CHCl_3$.
Methyl	110°	169° (11 mm.)	+ 39·4°
Ethyl	88	178 (13 mm.)	+ 35·1
*iso*Propyl	73	170 (10 mm.)	+ 35·3
*iso*Butyl	83	184 (11 mm.)	+ 33·9
*iso*Amyl	liquid	199 (11 mm.)	+ 34·2
Allyl	„	186 (10 mm.)	+ 34·3

The analytical data are recorded in Dr. W. Müller's thesis (Zürich, 1923).

Allyl Carbonate.—The oil obtained by the action of carbonyl chloride upon allyl alcohol is mixed with water, when two oily layers separate. The heavy oil is allyl chloroformate, which boils at 110°, not 180° as stated by Thiele and Dent (*Annalen*, 1880, **205**, 227; 1898, **302**, 269). The light oil on distillation yields *allyl carbonate*, b. p. 166°/730 mm., as a mobile liquid of unpleasant odour (Found: C = 59·03; H = 7·28. $C_7H_{10}O_3$ requires C = 59·15; H = 7·04 per cent.).

The physiological action of these camphorylcarbamates was examined with the hope that they would produce the combined

effects of camphor and the urethanes. The investigation was undertaken by Prof. Loewy in the laboratories of the Aktiengesellschaft für Anilinfabrikation, Berlin. He reported that their pronounced poisonous action renders these compounds unsuitable for practical application. Administered to dogs in doses of 0·3 gram per kilogram of body-weight, they had no marked action on the heart, but induced slow respiration, and sleep suddenly interrupted by strong convulsions.

THE SWISS TECHNICAL HIGH SCHOOL,
ZURICH.

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V.—*The Determination of Surface Tension from the Maximum Pressure in Bubbles. Part II.*

By SAMUEL SUGDEN.

SOME time ago (T., 1922, **121**, 858) the author discussed the theory of the method of maximum bubble pressure and described a simple apparatus by means of which determinations of the surface tension of water and benzene had been made. Measurements of the surface tension of some twenty different substances at temperatures up to 300° have now been carried out by this method. The results of these experiments will be discussed in subsequent papers; the present communication describes an improved form of apparatus which has been evolved during this investigation and outlines a much simpler method of calculating the surface tension from the observed data.

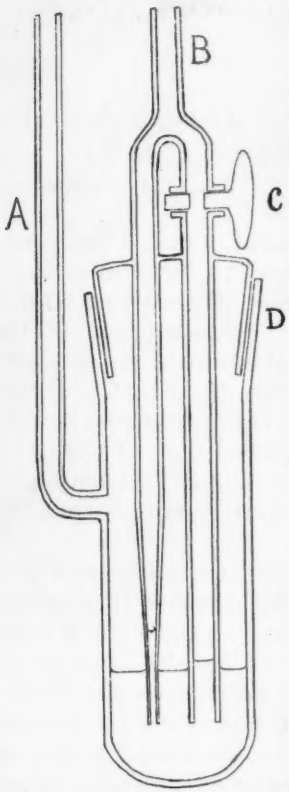
1. *Description of Apparatus.*—The apparatus consists essentially of three parts, the vessel holding the liquid under examination (referred to below as the bubbler), a pressure gauge, and a small mercury aspirator. The improved form of bubbler is shown in Fig. 1. The side tube, *A*, is connected to the gauge and aspirator. Air (dried if necessary) enters the tube *B* and passes through the capillary if tap *C* is closed but through the wide tube if *C* is open. The ground joint at *D* and the tap *C* must fit well, as no lubricant can be used except the substance under investigation, and in many cases when this is solid at the ordinary temperature one has to rely on the unlubricated joint. Fortunately, the pressure differences concerned are slight and a small leak can be neutralised by a rather more rapid flow of mercury in the aspirator.

The apparatus as supplied by the makers * is fitted with the

* The bubblers and gauge were supplied by Scientific Supplies Ltd., 52, Hatton Garden, E.C.1.

two inner tubes protruding about an inch below the stopper. A suitable length of tube of 3 to 4 mm. diameter is cut with the lower end of sharp cross-section normal to the axis of the tube and is sealed on to the limb bearing the stopcock. A length of 2 mm. tube is then sealed on to the other limb and is drawn out into a suitable capillary, which is cut off level with the end of the wide tube. After a little practice, the size of capillary needed can be estimated by the eye. The best test is to set up the apparatus and take a rough reading with the aid of benzene. A gauge containing absolute alcohol being used, the capillary is satisfactory if bubbles are formed with a gauge reading of not less than 4 cm. and not more than 10 cm. The upper limit corresponds to tubes with a diameter of 0·005 cm.; smaller tubes are difficult to work with, as they are too readily blocked by particles of dust.

FIG. 1.



The water gauge used in the earlier experiments was very troublesome and required continual cleaning to give trustworthy readings. Absolute alcohol tinted with magenta was therefore substituted for the water and the gauge was enclosed in a water-jacket. The density of the sample of alcohol used was determined at 10°, 20°, and 30°, and a table constructed to convert gauge readings at any temperature within these limits into dynes/cm.^{2}.

The mercury aspirator described in the previous paper has been found satisfactory. For smooth working, it is important to see that there is an unbroken column of mercury between the tap and the end of the capillary.

2. *Method of Calculation.*—It was shown in the previous paper that

$$\gamma = \frac{P}{2(1/X_1 - 1/X_2)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where γ is the surface tension in dynes/cm. and P is the difference between the pressures required to liberate bubbles from the two

tubes measured in dynes/cm.^{2}. X_1 and X_2 are functions of a^2 and r_1 and r_2 where

$$a^2 = \frac{2\gamma}{g(D-d)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Here g = acceleration due to gravity = 981 cm./sec.^{2}, D and d are the densities of the liquid and vapour, respectively, and r_1 and r_2 are the radii of the two tubes. In the paper referred to above, equation (1) was solved by a method of successive approximations using a table giving the ratio X/r for a number of values of r/a.

Now (1) may be written

$$\gamma = A \,.\, P \,.\, f(r_1, r_2, a) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

As a increases and r_1 decreases, $f\,(r_1, r_2, a)$ tends to unity, and for the sizes of tubes used and for most organic liquids at temperatures up to the boiling point it is never greater than 1·04. Further, since r_1 is small, X_1 varies very little from liquid to liquid, so that we can regard the factor multiplying AP as a function of r_2 and a, or as a function of r_2 and the quantity gD/P, which is nearly proportional to a^2. It has been found that, within the limits specified below, equation (1) can be replaced by

$$\gamma = A \,.\, P\left(1 + 0{\cdot}69 r_2 \frac{gD}{P}\right) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

when r_2 is measured in cm.

The limits within which this formula holds were tested by calculating a number of values by (4) and by the general method given in the previous paper. In Table I, the column headed Surface Tension (1) gives the values calculated by equation (4). In these calculations, $D = 1$.

TABLE I.

r_1 cm.	r_2 cm.	P dyn./cm.^{2}.	a^2 mm.^{2}	$1+0{\cdot}69 r_2 \frac{gD}{P}$	Surface tension. (1) dyn./cm.	(2) dyn./cm.	Diff.
0·005	0·100	6540	3·546	1·0104	17·39	17·39	0
0·005	0·200	6540	3·493	1·0207	17·14	17·12	0·02
0·010	0·100	3270	3·774	1·0207	18·51	18·53	0·02
0·010	0·200	3270	3·658	1·0414	17·94	17·92	0·02
0·005	0·100	19620	10·56	1·0035	51·80	51·78	0·02
0·010	0·200	9810	11·185	1·0138	54·85	54·86	0·01

For organic liquids at the boiling point, a^2 is rarely much less than 4 mm.^{2}. Hence from the first four lines of Table I it is seen that formula 4 holds with an accuracy of 1 part in 1000 when r_1 is less than 0·010 cm. and r_2 is not greater than 0·20 cm. These limits are determined by practical considerations. If r_1 is greater than 0·010 cm., the readings on the gauge are too small to give

accurate values for the surface tension; on the other hand, tubes smaller than 0·005 cm. are very easily blocked by particles of dust.

3. *Calibration and Calculations.*—The direct measurement of the radius of the capillary as described in the previous paper is somewhat tedious and is scarcely practicable in a series of measurements, as the capillaries may be broken when the apparatus is being cleaned. The surface tension of benzene at 20° is now known with accuracy and may be taken as 28·88 dynes/cm. (Richards and Carver, *J. Amer. Chem. Soc.*, 1921, **43**, 827; Harkins and Brown, *ibid.*, 1919, **41**, 499). This value has been confirmed by the author by two methods, that of capillary rise (T., 1921, **119**, 1483), and by the method of maximum bubble pressure (*loc. cit.*). Hence benzene may be used as a convenient reference liquid. It has also been found that traces of common impurities such as thiophen have no appreciable effect on its surface tension and a suitable specimen may be prepared by freezing "crystallisable" benzene once, rejecting about one-third as the more fusible fraction, fractionally distilling the remainder through a column of glass beads, and collecting the fraction boiling from 80° to 80·5°. The purified benzene has (usually) been dried and stored over sodium, but this has been found unnecessary. To test this point, an experiment was made using benzene which had been dried over sodium for ten weeks. The surface tension of the dry liquid was first determined, a drop of water added, and the measurements were repeated; a further set of readings was made after the benzene and water had been in contact for forty-eight hours. As the figures below show, moisture has no appreciable effect on the surface tension as measured by the method of maximum bubble pressure.

	Surface tension in dynes/cm.		
Temp.	Dry.	Water added.	After 48 hours.
21°	28·81	28·74	28·78
39	26·33	26·38	26·36
61	23·65	23·65	23·54

Table II gives the surface tension of benzene at every degree from 10° to 30°. It is calculated by the formula

$$\gamma = 70{\cdot}26\left(1 - \frac{\theta}{560}\right)^{1{\cdot}20} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

which, as will be shown in a subsequent paper, reproduces the experimental data on this substance with accuracy from the freezing point to the critical point. This table enables benzene to be used as standard liquid at the laboratory temperature.

TABLE II.

Temp.	10°	11°	12°	13°	14°	15°	16°
γ dynes/cm.	30·19	30·05	29·92	29·79	29·66	29·53	29·40
Temp.	17°	18°	19°	20°	21°	22°	23°
γ dynes/cm.	29·27	29·14	29·01	28·88	28·75	28·62	28·49
Temp.	24°	25°	26°	27°	28°	29°	30°
γ dynes/cm.	28·36	28·23	28·10	27·97	27·84	27·71	27·58

As an example of the method of calculation, a few figures for benzene are given below in detail.

Apparatus 3 . $r_2 = 0{\cdot}159$ cm. At 20°, with benzene, $H = 10{\cdot}90$ cm. H is the observed difference in gauge readings for the wide and narrow tubes. Gauge temperature 14°; at this temperature the factor to convert gauge readings into dynes/cm.^{2} is 780·5, whence $P = 8508$ dynes/cm.^{2}. If ϕ represents the correction factor, so that

$$\phi = 1 + 0{\cdot}69 r_2 \frac{gD}{P} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

then, since $D = 0{\cdot}877$, $\phi = 1{\cdot}0111$, and from (4) $A = 0{\cdot}003358$, the required constant for this particular instrument. With this value of A, observations on benzene at other temperatures are calculated below.

Temp.	H cm.	Gauge temp.	Gauge factor.	P dynes/cm.^{2}.	D gm./c.c.	ϕ.	γ. dynes/cm.
13·5°	11·20	12·5°	781·7	8757	0·885	1·011	29·72
34·5	10·18	14	780·5	7943	0·862	1·012	26·98
72	8·34	14	780·5	6510	0·819	1·0135	22·15

P is obtained by multiplying H by the gauge factor, ϕ is then calculated by (6), and the surface tension by (4), the value found above for the constant A being used.

The author is indebted to the Research Fund Committee of this Society for a grant which has largely defrayed the cost of this investigation.

BIRKBECK COLLEGE,
UNIVERSITY OF LONDON.

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VI.—*The Variation of Surface Tension with Temperature and some Related Functions.*

By Samuel Sugden.

It is well known that a linear relationship between surface tension and temperature can only be used over small ranges of temperature. In 1894, van der Waals (*Z. physikal. Chem.*, **13**, 716) gave two formulæ connecting surface tension and temperature which involve the critical constants.

$$\gamma = K_1\theta_c V_c^{-\frac{2}{3}}(1-m)^B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$= K_2\theta_c^{\frac{1}{3}}p_c^{\frac{2}{3}}(1-m)^B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Here θ_c, V_c, and p_c are the critical temperature, volume, and pressure, m is the reduced temperature, and K_1, K_2, and B are universal constants.

Ferguson (*Phil. Mag.*, 1916, [vi], **31**, 37) has suggested the formula

$$\gamma = \gamma_0(1-bt)^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where n varies from substance to substance. This variation is not large, the values of n for non-associated liquids ranging from 1·192 to 1·248, and Ferguson states that the mean value 1·21 gives satisfactory results in most cases.

More recently, Macleod (*Trans. Faraday Soc.*, 1923, **19**, 38) has shown that

$$\gamma = C(D-d)^4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where C is a constant for a given liquid over a large range of temperature. Here D is the density of the liquid and d that of the vapour. In a paper recently read before the Faraday Society (2nd July, 1923), Ferguson has shown by eliminating $1-m$ between (3) and Katayama's modification of the Ramsay-Shields equation, namely,

$$\gamma\left(\frac{M}{D-d}\right)^{\frac{2}{3}} = A\theta_c(1-m) \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

(*Sci. Rep. Tohoku Imp. Univ.*, 1916, **4**, 373) that Macleod's relation results if $n = 1{\cdot}20$. Hence if Macleod's relation holds, Ferguson's equation reduces to that of van der Waals and the universal constant B has the value 1·20.

This leads us to inquire whether it is necessary to have a variable exponent to reproduce the experimental figures with sufficient accuracy or whether a formula of the van der Waals type is adequate. We may rewrite (1)

$$\gamma = \gamma_0(1-m)^{1\cdot 20} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$\text{where } \gamma_0 = K_1\theta_c V_c^{-\frac{2}{3}} = K_2\theta_c^{\frac{1}{3}}p_c^{\frac{2}{3}} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

By applying (6) to the experimental data we can test the constancy of B, and then from the values of γ_0 and the critical constants see if K_1 and K_2 are universal constants.

The most important measurements of surface tension up to the neighbourhood of the critical temperature are those contained in the classical paper of Ramsay and Shields (*Phil. Trans.*, 1893, **184**, 647). It is, however, now certain that the surface tensions obtained by these workers are too low because of an inadequate correction for the capillary rise in the wider tube. Fortunately, sufficient experimental data are recorded in this paper to enable one to calculate the necessary correction.

Details of the calculation of this correction are given in an appendix to the present paper, but the method employed may be described briefly here. In the first place, measurements were made of the surface tension of benzene and chlorobenzene up to the boiling point by the method of maximum bubble pressure (this volume, p. 27). To these figures a formula of type (6) was fitted and the surface tensions at temperatures a few degrees above the boiling point were obtained by extrapolation. From these and the capillary rise observed by Ramsay and Shields the radius of the wide tube was calculated, using the theory of the method of capillary rise worked out by the author two years ago (T., 1921, **119**, 1483). Once this radius is determined, the corrected values of the surface tension can be calculated.

To save labour, the corrected surface tensions have been calculated at 30° intervals instead of the 10° intervals given by Ramsay and Shields. Further, it should be noted that these corrected surface tensions are calculated from the observed values of the capillary rise, whilst Ramsay and Shields's figures are deduced from a smoothed value. It seemed preferable to allow the figures to be burdened with the experimental error rather than to use an arbitrarily smoothed curve, since the main object of the work was to test whether formula (6) was capable of representing the experimental figures with sufficient accuracy.

A further check on the values for benzene, chlorobenzene, and carbon tetrachloride was obtained from the observations of Walden and Swinne (*Z. physikal. Chem.*, 1912, **79**, 700). These workers employed the method of capillary rise and constructed an apparatus with one tube of large diameter (2—3 cm.), so that the correction for capillary rise in this tube was very small and could be calculated accurately. They deduced the radius of the capillary from observations on benzene, using Ramsay and Shields's figures for the surface tension of this substance, and found a radius of 0·1930 mm. If this figure is recalculated using accurate values for the surface

tension of benzene, a much higher value is obtained, as is shown below. The radius of the capillary is given by the equation

$$r = \frac{2\gamma}{981 \cdot 7h(D - d)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Benzene.

Temp.	h cm.	$D-d$ gm./c.c.	γ. dynes/cm.	r mm.
20°	3·374	0·8787	28·88	0·1985
30	3·237	0·8680	27·59	0·2000
40	3·134	0·8569	26·31	0·1996
50	3·015	0·8455	25·03	0·1999

Similarly, from the accurate values of Richards and Carver (*J. Amer. Chem. Soc.*, 1921, **43**, 827) for the surface tension of toluene and carbon tetrachloride two more values of r can be obtained, namely, toluene, $r = 0{\cdot}1991$ mm., carbon tetrachloride, $r = 0{\cdot}1995$ mm. Taking the mean figure 0·1994 cm., the figures of Walden and Swinne can be corrected by multiplying by $0{\cdot}1994/0{\cdot}1930 = 1{\cdot}0335$. This simple method of correction can be adopted in this case because the correction for the wide tube is so small and would not be altered appreciably if one employed the corrected surface tension instead of the old figure to determine the magnitude of the capillary rise in this tube.

It is interesting to note that Walden and Swinne made a direct determination of the radius of the capillary by means of a mercury thread. They found a value of 0·1978 mm. which, however, they disregarded, adopting the figure 0·1930 in all their calculations.

Having obtained the corrected figures for the surface tension, the next step was to test equation (6). This was done by plotting $\gamma^{\frac{2}{3}}$ against the temperature, when, as is seen in Fig. 1, the points for any one liquid were found to lie on a straight line. From the intercepts of this line on the axes of the graph the constants of (6) were calculated and the formula was then used to predict the surface tensions.

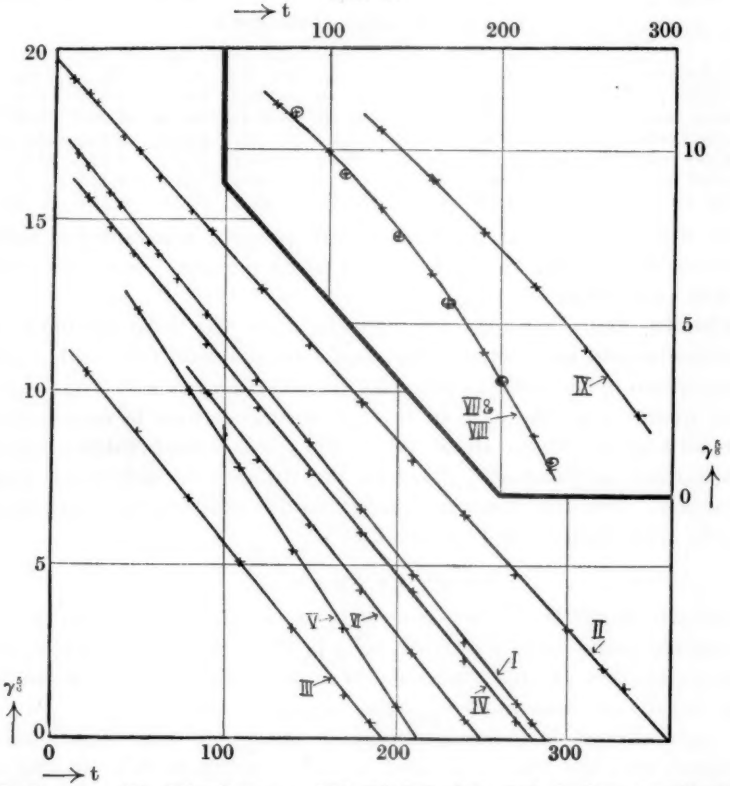
As will be seen from the table on pages 37, 38, the observed figures are reproduced with considerable accuracy in the case of the six normal liquids benzene, chlorobenzene, diethyl ether, carbon tetrachloride, methyl formate, and ethyl acetate. The greatest differences between observed and calculated figures are found with chlorobenzene, but these differences are irregularly distributed and could not be eliminated by giving to n another value than 1·20. In the column headed "observer," R. & S. stands for Ramsay and Shields, W. & S. for Walden and Swinne, R. & C. for Richards and Carver, and S. for Sugden.

The three associated liquids do not obey this law, as can be

seen in Fig. 1, where methyl and ethyl alcohols and acetic acid give lines of marked curvature.

The next test is to compare the values of the critical temperature deduced from the surface tension measurements with the figures obtained by direct observation. These are shown in the table below; the critical temperatures are those given by Young (*Proc. Roy. Soc. Dublin*, 1910, **12**, 374).

FIG. 1.



I. *Benzene.* II. *Chlorobenzene.* III. *Diethyl ether.* IV. *Carbon tetrachloride.* V. *Methyl formate.* VI. *Ethyl acetate.* VII. *Methyl alcohol* +. VIII. *Ethyl alcohol* ⊕. IX. *Acetic acid.*

Substance.	Critical temperature. Calc.	Obs.	Diff.
Benzene	287°	288·5°	−1·5°
Chlorobenzene	358	359·2	−1·2
Diethyl ether	193	193·8	−0·8
Methyl formate	212	214	−2
Ethyl acetate	249	250·1	−1·1
Carbon tetrachloride	280	283·1	−3·1

It will be seen that the predicted critical temperatures are usually a degree or two below the observed value, but in general there is

good agreement, although not so good as that obtained by Ferguson (*loc. cit.*). This, however, is only to be expected, as his formula allows n to be varied slightly, and should give a closer fit.

The next point which arises is the relationship between the critical constants and γ_0 which van der Waals deduced from the theory of corresponding states. In the table below, the critical data are due to Young (*loc. cit.*) and K_1 and K_2 are the constants in equations (1) and (2).

Van der Waals's Constants.

Substance.	γ_0.	θ_c.	p_c atm.	d_c gm./c.c.	V_c c.c.	K_1.	K_2.
Benzene	70·26	561·5	47·89	0·3405	256·1	5·047	0·646
Chlorobenzene	70·33	673·2	44·64	0·3654	307·8	4·763	0·638
Diethyl ether	55·96	466·8	35·61	0·2625	281·9	5·155	0·667
Carbon tetrachloride	66·27	556·2	44·98	0·5576	276·1	5·171	0·637
Methyl formate	75·85	487	59·25	0·3489	172·0	4·818	0·635
Ethyl acetate	65·24	523·1	38·00	0·3077	286·0	5·414	0·716

It will be seen that K_1 and K_2 are roughly constant for these six substances, but vary by several units per cent. from one substance to another.

Finally, there remains for consideration the relation between surface tension and density discovered by Macleod (*loc. cit.*). The last column in the table on pages 37, 38 gives the value of $\gamma^{\frac{1}{4}}/(D - d)$. This quantity in the case of the six normal liquids is remarkably constant up to within about 40° of the critical temperature, where the surface tensions and densities are difficult to determine with accuracy. For the three associated liquids this function increases slowly with increasing temperature.

Experimental.

Details of the measurements on benzene have been given in the preceding communication (this vol., p. 27). Measurements of the surface tension of chlorobenzene were made by the same methods and details of these measurements are given below.

Purification.—A good commercial specimen was fractionally distilled and the specimen used boiled steadily at 131° (corr.) at 750 mm.

Apparatus.—Two instruments were used: No. 1, for which $r_2 = 0{\cdot}163$ cm. and $A = 0{\cdot}003736$, and No. 3, for which $r_2 = 0{\cdot}159$ cm. and $A = 0{\cdot}003333$.

Densities are due to Young (*loc. cit.*).

Temp.	P dynes/cm.^{2}.	$D-d$ gm./c.c.	ϕ.	γ dynes/cm.	
12°	9070	1·118	1·014	34·36	
50	7860	1·073	1·016	29·83	App. 1
93	6573	1·025	1·018	24·99	
81	7708	1·039	1·016	26·10	App. 3
123	6377	0·991	1·018	21·63	

Summary.

(1) The surface tension measurements of Ramsay and Shields and of Walden and Swinne have been corrected.

(2) For six non-associated liquids it has been shown that the variation of surface tension with temperature is represented accurately by the formula $\gamma = \gamma_0(1 - m)^{1\cdot20}$, where m is the reduced temperature and γ_0 a constant.

(3) The relations between γ_0 and the critical constants predicted by van der Waals have been shown to hold approximately.

(4) Macleod's relationship between surface tension and density is found to hold accurately for non-associated liquids up to about 40° below the critical temperature.

TABLE.

Temp.	Observer.	γ obs.	γ calc.	Diff.	$D-d$.	$\frac{\gamma^{\frac{1}{4}}}{D-d}$
			I. Benzene.			
13·5°	S.	29·72	29·74	+0·02	0·8857	2·637
20	R. & C.	28·88	28·88	±0·00	0·8787	2·638
20·5	W. & S.	28·91	28·82	−0·09	0·8782	2·641
21	S.	28·74	28·75	+0·01	0·8777	2·638
32·5	W. & S.	27·30	27·27	−0·03	0·8653	2·642
34·5	S.	26·98	27·11	+0·13	0·8631	2·641
39	S.	26·36	26·44	+0·08	0·8581	2·641
41·5	W. & S.	26·08	26·12	+0·04	0·8553	2·642
54·8	W. & S.	24·28	24·43	+0·15	0·8400	2·642
61	S.	23·61	23·65	+0·04	0·8330	2·647
72	S.	22·15	22·26	+0·11	0·8207	2·643
90	R. & S.	20·13	20·05	−0·08	0·8006	2·646
120	,,	16·42	16·45	+0·03	0·7616	2·643
150	,,	13·01	12·97	−0·04	0·7166	2·650
180	,,	9·56	9·64	+0·08	0·6657	2·641
210	,,	6·45	6·48	+0·03	0·6011	2·651
240	,,	3·47	3·59	+0·12	0·5137	2·657
270	,,	1·05	1·06	+0·01	0·3696	2·739
280	,,	0·36	0·37	+0·01	0·2305	3·372
			II. Chlorobenzene.			
12	S.	34·36	34·21	−0·15	1·118	2·166
18·7	W. & S.	33·35	33·42	+0·13	1·108	2·173
24·1	,,	32·85	32·78	−0·07	1·102	2·172
41	,,	30·78	30·79	+0·01	1·083	2·174
50	S.	29·83	29·75	−0·08	1·073	2·178
52·2	W. & S.	29·38	29·49	+0·11	1·070	2·175
62·1	,,	28·20	28·34	+0·14	1·059	2·176
81	S.	26·10	26·19	+0·09	1·039	2·176
93	,,	24·99	24·83	−0·16	1·025	2·182
123	,,	21·63	21·50	−0·13	0·991	2·176
150	R. & S.	18·55	18·57	+0·02	0·9545	2·174
180	,,	15·40	15·40	±0·00	0·9122	2·172
210	,,	12·16	12·35	+0·19	0·8622	2·166
240	,,	9·30	9·41	+0·11	0·8054	2·168
270	,,	6·43	6·61	+0·18	0·7341	2·169
300	,,	4·05	4·01	−0·04	0·6442	2·202
320	,,	2·39	2·25	−0·14	0·5628	2·210
333	,,	1·63	1·46	−0·17	0·4914	2·299

Temp.	Observer.	γ obs.	γ calc.	Diff.	$D-d$.	$\frac{\gamma^{\frac{1}{3}}}{D-d}$.
			III. Diethyl ether.			
20	R. & C.	17·01	17·04	+0·03	0·7109	2·857
50	R. & S.	13·69	13·56	−0·13	0·6713	2·865
80	,,	10·25	10·23	−0·02	0·6286	2·850
110	,,	7·00	7·06	+0·06	0·5707	2·865
140	,,	4·00	4·12	+0·12	0·4936	2·865
170	,,	1·42	1·51	+0·09	0·3785	2·884
185	,,	0·40	0·43	+0·03	0·2698	2·947
			IV. Carbon tetrachloride.			
20	R. & C.	26·95	26·80	−0·15	1·593	1·429
21·1	W. & S.	26·71	26·66	−0·05	1·591	1·428
33·0	,,	25·22	25·20	−0·02	1·567	1·429
45·9	,,	23·63	23·63	±0·00	1·540	1·432
90	R. & S.	18·51	18·40	−0·11	1·4475	1·433
120	,,	14·95	14·96	+0·01	1·3740	1·431
150	,,	11·46	11·66	+0·20	1·2914	1·425
180	,,	8·50	8·51	+0·01	1·1945	1·429
210	,,	5·67	5·55	−0·12	1·0687	1·444
240	,,	2·64	2·83	+0·19	0·8980	1·419
270	,,	0·49	0·55	+0·06	0·5955	1·405
			V. Methyl formate.			
50	R. & S.	20·48	20·35	−0·13	0·9251	2·300
80	,,	15·95	15·92	−0·03	0·8698	2·297
110	,,	11·77	11·66	−0·11	0·8048	2·301
140	,,	7·63	7·69	+0·06	0·7156	2·322
170	,,	3·96	4·03	+0·07	0·6081	2·319
200	,,	0·92	0·90	−0·02	0·4131	2·37
			VI. Ethyl acetate.			
90	R. & S.	15·74	15·67	−0·07	0·8065	2·470
120	,,	12·08	12·19	+0·11	0·7580	2·450
150	,,	8·85	8·87	+0·02	0·7005	2·462
180	,,	5·70	5·75	+0·05	0·6265	2·467
210	,,	2·94	2·90	−0·04	0·5232	2·50
240	,,	0·50	0·50	±0·00	0·3278	2·56
			VII. Methyl alcohol.			
20	R. & C.	22·61			0·7910	2·757
70	R. & S.	18·50			0·7445	2·787
100	,,	15·73			0·7100	2·804
130	,,	12·66			0·6676	2·826
160	,,	9·34			0·6141	2·846
190	,,	5·56			0·5369	2·866
220	,,	1·95			0·4036	2·928
230	,,	0·77			0·3223	2·905
			VIII. Ethyl alcohol.			
20	R. & C.	22·27			0·7888	2·755
80	R. & S.	17·97			0·7360	2·797
110	,,	14·49			0·7008	2·785
140	,,	11·34			0·6516	2·817
170	,,	7·85			0·5920	2·828
200	,,	4·26			0·5050	2·845
230	,,	0·95			0·3415	2·891
			IX. Acetic acid.			
130	R. & S.	17·05			0·9190	2·211
160	,,	14·21			0·8729	2·224
190	,,	11·45			0·8245	2·231
220	,,	8·71			0·7643	2·248
250	,,	5·70			0·6841	2·258
280	,,	2·83			0·5685	2·281

Appendix. Correction of Ramsay and Shields's Data.

The apparatus used by Ramsay and Shields consisted of a capillary tube mounted concentrically in a wider tube. It is very difficult to deal with this case mathematically, but a complete solution of the analogous problem of two communicating tubes has been given by the author (T., 1921, **119**, 1483). Since the correction to be calculated is small (about 5 per cent.), it would seem that the quantity required might be calculated in the following manner. Using accurate data for some standard liquid and the observed capillary rise recorded by Ramsay and Shields, one can calculate the radius of an equivalent wide tube which, if it were placed in communication with the capillary and not around it, would have the same effect as Ramsay and Shields's concentric tube. Then by the aid of the tables in the paper referred to above, the observations of these workers can be recalculated, as the radii of both tubes have been determined. The assumption made here is that an external tube which has the same effect as a concentric tube at one particular surface tension has the same effect as the concentric tube at all surface tensions. This assumption, whilst perhaps not rigidly true, must be so to a first approximation, and since the total correction for the capillary rise in the wide tube is about 10 per cent. at the lower temperatures and diminishes to zero at the critical temperature, it does not seem likely that any large error will result if this method is adopted. What may be termed "internal evidence" for the truth of this hypothesis may be found in the table on pages 37, 38, where it will be seen that the corrected data obtained in this manner are in harmony with the values found by other observers.

The standard liquids chosen for the determination of the radius of the wide tube were benzene and chlorobenzene. From a series of measurements by the method of maximum bubble pressure, it was found that the surface tensions of these liquids could be represented by the formulæ

$$\text{Benzene } \gamma = 70{\cdot}26\left(1 - \frac{\theta}{560}\right)^{1{\cdot}2} \quad . \quad . \quad . \quad (9)$$

$$\text{Chlorobenzene } \gamma = 70{\cdot}33\left(1 - \frac{\theta}{631}\right)^{1{\cdot}2} \quad . \quad . \quad . \quad (10)$$

where θ is the absolute temperature. From (9) it is found that for benzene at 90° $\gamma = 20{\cdot}05$ dynes/cm. At this temperature, $D - d = 0{\cdot}8006$, whence $a^2 = 5{\cdot}105$ mm.^{2}. Now for an apparatus with two communicating tubes

$$1/b_1 - 1/b_2 = H/a^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where b_1 and b_2 are the radii of curvature at the lowest points of the liquid surface in the capillary and wide tubes, respectively. To calculate $1/b_1$, we proceed as follows. In Ramsay and Shields's apparatus, $r_1 = 0{\cdot}012935$ cm., hence $r_1/a = 0{\cdot}05275$. From the table in the author's paper referred to above, this corresponds to $r_1/b = 0{\cdot}9989$, whence $1/b = 77{\cdot}22$. The capillary rise for benzene found by Ramsay and Shields at this temperature was $H = 3{\cdot}460$ cm., from which $H/a^2 = 67{\cdot}78$ and $1/b_2 = 9{\cdot}44$. By the aid of the table connecting r/a and r/b, it was found that for this value of a^2 $1/b = 9{\cdot}50$ when $r_2 = 0{\cdot}099$ cm. and $1/b = 9{\cdot}39$ when $r_2 = 0{\cdot}100$ cm., whence by interpolation $r_2 = 0{\cdot}0996$ cm.

Similar calculations were made for benzene at 120° and for chlorobenzene at 150° and 180° with the following results.

	Benzene.		Chlorobenzene.		
Temp.	90°	120°	150°	180°	
r_2 cm.....	0·100	0·096	0·096	0·097	Mean 0·097 cm.

Using this value of r_2, any of the observations of Ramsay and Shields may be recalculated by the method of successive approximations detailed in the author's 1921 paper (*loc. cit.*). This would involve a very laborious series of calculations which can be avoided in the following manner.

Since

$$a^2 = \frac{2\gamma}{g(D-d)} = \frac{H}{1/b_1 - 1/b_2} \quad . \quad . \quad . \quad (12)$$

we can write

$$\gamma = H(D-d)\phi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where

$$\phi = \frac{g}{2(1/b_1 - 1/b_2)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Now ϕ is a function of r_1, r_2, and a^2, and for a given apparatus, where r_1 and r_2 are fixed, is a function of H only. Hence if ϕ is calculated for a few values of H, intermediate values can be obtained by interpolation. The table below gives corresponding values of ϕ and H for the range required.

H	0·10	0·15	0·20	0·40	0·70	1·00
ϕ	6·828	6·839	6·881	6·881	7·108	7·158
H	1·50	2·00	3·0	4·0	5·0	∞
ϕ	7·208	7·233	7·259	7·271	7·280	7·321

From these values a curve was drawn to give intermediate values of ϕ and the corrected surface tensions were calculated by equation (13). A few examples are given below.

Liquid.	Temp.	H.	$D-d$.	ϕ.	γ corr.	γ R. & S.
Benzene	90°	3·460	0·8006	7·265	20·13	19·16
,, ...	240	0·945	0·5137	7·155	3·47	3·41
Chlorobenzene ...	150	2·68	0·9545	7·251	18·55	17·67
,, ...	320	0·60	0·5628	7·084	2·39	2·35

The last column in the table gives the surface tension calculated by Ramsay and Shields. It will be seen that the corrected figures are about 1 dyne/cm. higher at the lower temperatures, the difference diminishing as the temperature rises.

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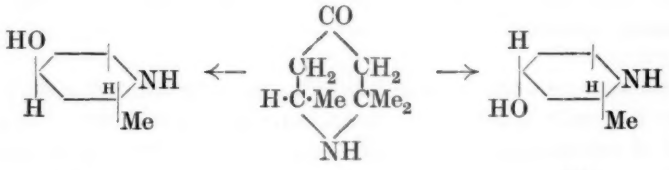
VII.—*Stereoisomerism and Local Anæsthetic Action in the β-Eucaine Group. Resolution of β- and* iso-*β-Eucaine.*

By HAROLD KING.

WHEN the work detailed below was begun, there was no case known where the dextro- and lævo-modifications of any of the local anæsthetics had been examined for their relative anæsthetic properties. In the meantime, however, Gottlieb has described (*Arch. Exp. Path. Pharm.*, 1923, **97**, 113) the relative anæsthetic effect of *dl*- and *l*-cocaine and of *d*- and *l*-ψ-cocaine which have recently become available. The present author chose β-eucaine and stovaine as representatives of synthetic local anæsthetics suitable for resolution. So far, no crystalline salts have been obtained from stovaine with optically active acids, but β-eucaine forms a series of such salts which crystallise extremely well.

Vinyldiacetonamine (2 : 2 : 6-trimethyl-4-piperidone) (I) on reduction with sodium amalgam gives two racemic alcohols, α- and β-vinyldiacetonalkamines (4-hydroxy-2 : 2 : 6-trimethylpiperidine) (II and III) (Harries, *Annalen*, 1897, **294**, 336),



(II.) (I.) (III.)

each of which on benzoylation gives a mono-*O*-benzoyl derivative. The conditions necessary for the preparation of N-*benzoyl*-β-*vinyldi*-

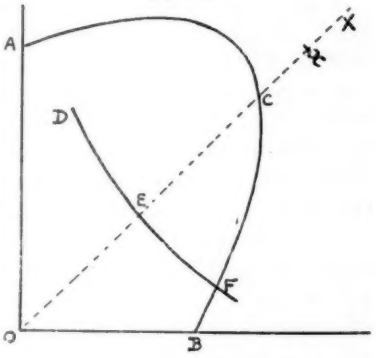
acetonalkamine, ON-*dibenzoyl*-β-*vinyldiacetonalkamine*, and ON-*dibenzoyl*-α-*vinyldiacetonalkamine* are described in the experimental portion of this paper. The constitution of *N*-benzoyl-β-vinyldiacetonalkamine, which was only obtained in small quantity, follows because it is different from the product of benzoylation of *O*-benzoyl-β-vinyldiacetonalkamine. *O*-Benzoyl-α-vinyldiacetonalkamine is known as β-eucaine, whilst for convenience of reference *O*-benzoyl-β-vinyldiacetonalkamine will be called hereinafter *iso*-β-eucaine. This latter base is unrecorded in Beilstein's "Handbuch" or Richter's "Lexicon," but a brief description of it may be found in D.R.-P. 95620 and in a paper by Vinci (*Pfluger's Archiv*, 1897, **149**, 220). Each of these bases has been resolved and a comparison made of their physiological properties. In this way, it has not only been possible to effect a comparison of two diastereoisomerides, β-eucaine and *iso*-β-eucaine, but also of two pairs of enantiomorphs, *d*- and *l*-β-eucaine and *d*- and *l*-*iso*-β-eucaine.

The resolution of β-eucaine and of *iso*-β-eucaine both present somewhat novel features. The normal salts of β-eucaine with d-*camphoric*, d-*tartaric*, and l-*malic* acid are partial racemates. With *d*-camphor-10-sulphonic acid, the stable salt over the range between room temperature and below zero is also a partial racemate, dl-β-*eucaine* d-*camphor*-10-*sulphonate* crystallising in massive tablets containing a molecule of alcohol of crystallisation, but it has been found possible to resolve this salt by means of the more soluble active forms which are unstable in respect of the partial racemate. Ladenburg found (*Ber.*, 1894, **27**, 75) that when he evaporated solutions of β-pipecoline tartrate at water-bath temperatures the salt which separated was the partial racemate, but when the solutions were evaporated at the ordinary temperature he obtained the salt containing a preponderance of *l*-pipecoline. In a later paper (*Ber.*, 1898, **31**, 527), he added a postscript showing that crystallisation of quinine methylsuccinate between 0° and 30° yielded the partial racemate, but above 70° an acid was obtained having a rotation of $+0{\cdot}1°$ in 10 per cent. solution. The present case differs from these in that resolution has been effected *within* the transition interval where the partial racemate is the most stable form.

A reference to the accompanying isothermal solubility diagram, which is purely qualitative, will render the phenomena observed easier of interpretation. *A* and *B* are the solubilities, respectively, of *d*-β-eucaine *d*-camphorsulphonate and *l*-β-eucaine *d*-camphorsulphonate at room temperature in a constant amount of the solvent, alcohol in this case. The curve joining these points being continuous expresses the solubility of the continuous series of mixed

crystals which are formed by these salts. The solubility curve of the partial racemate *dl*-β-eucaine *d*-camphorsulphonate, which is much less soluble, is represented by *DF*. A supersaturated solution of the partial racemate, point *x*, kept at temperatures between − 5° and + 30° will in general deposit the partial racemate, point *E*, as being the least soluble form. Owing, however, to the intervention of Ostwald's rule of the prior formation of less stable forms the solid deposited may not be the partial racemate but mixed crystals of the two optically active salts, not represented by the point *C*, but by some point in the region between *C* and *B* (not necessarily on *BC*, as the composition of the mixed crystals cannot be represented adequately on this type of diagram). If, however, the partial racemate makes its appearance at any time, as frequently happens, especially on keeping the solutions over-night, it is followed by rapid solution of the mixed crystals. Owing to the relatively sparing solubility of the partial racemate, even solutions which contain a preponderance of the *l*-β-eucaine *d*-camphorsulphonate and in which the process of resolution by fractional crystallisation has proceeded a considerable way towards completion, will deposit the partial racemate and thus negative the quantitative progress towards resolution. Beyond the point where *EF* and *CB* intersect the stability conditions are reversed. The relative stability of the various forms at higher temperatures has not been examined. The fact, however, that the partial racemate crystallises with 1 mol. of alcohol which is readily lost would suggest that at higher temperatures this form of the partial racemate would be unstable. By fractional crystallisation of the unstable forms it has been possible to isolate 54 per cent. of *l*-β-eucaine *d*-camphorsulphonate.

FIG. 1.



Owing to the formation of a continuous series of mixed crystals between the two active salts, it was not found possible to isolate the more soluble salt, *d*-β-eucaine *d*-camphorsulphonate. By the use, however, of *l*-camphor-10-sulphonic acid, kindly lent to the author by Professor C. S. Gibson of Guy's Hospital, the isolation of *d*-β-eucaine *l*-camphorsulphonate became an easy matter.

The chemical results with β-eucaine are tabulated below :

	l-β-Eucaine.	*d*-β-Eucaine.	*r*-β-Eucaine.
Base :			
Appearance	Columns	Columns	Plates or tablets
M. p.	57—58° corr.	57—58° corr.	70—71° corr.
Hydrochloride :			
Appearance	Rectangular plates	Rectangular plates	Small tablets
M. p.	244—245° corr.	244—245° corr.	277—279° corr.
$[\alpha]_D$	−13·0°	+13·1°	—
Picrate :			
Appearance	Prisms	—	Short rods
M. p.	198—199° corr.	—	231·5—232·5° corr.

A point which calls for remark is the melting point of *r*-β-eucaine base. A great variety of values is recorded in the literature. In D.R.-P. 97672, the value 78° is given, Vinci (*loc. cit.*) gives the two values 87° and 75° on the same page, whilst Parsons (*J. Amer. Chem. Soc.*, 1901, **23**, 885) gives the figure 91°. *r*-β-Eucaine prepared from its pure optically active components has m. p. 70—71° (corr.), the same as that of the commercial base and it seems likely that Parson's value 91° is a misprint for 71°.

iso-β-Eucaine forms an uncrystallisable salt with camphor-10-sulphonic acid, but its resolution is effected without great difficulty by means of *d*-α-bromo-π-camphorsulphonic acid. Here, again, the behaviour is somewhat unusual. The first time the author fractionated this salt from absolute alcohol the successive products of crystallisation showed steadily increasing rotations and eventually d-iso-β-*eucaine* d-*bromocamphorsulphonate* was isolated almost pure. When, however, a larger batch of material was submitted quite independently to the same process, the rotations fell and l-iso-β-*eucaine* d-*bromocamphorsulphonate* was isolated as the apparently least soluble salt. The matter is further complicated by the fact that *d-iso*-β-eucaine *d*-bromocamphorsulphonate crystallises with a molecule or less of water of crystallisation from alcoholic solutions. At first it was thought that this was the determining factor, but it seems that the anomalous behaviour is due to the approximately equal solubilities of the two salts and to the fact that they do not show any great tendency to form a difficultly separable series of mixed crystals. It was found, in working up the mother-liquors of the larger batch, that the successive crops of pure material isolated by repeated fractional crystallisation were almost alternatively dextro and lævo.

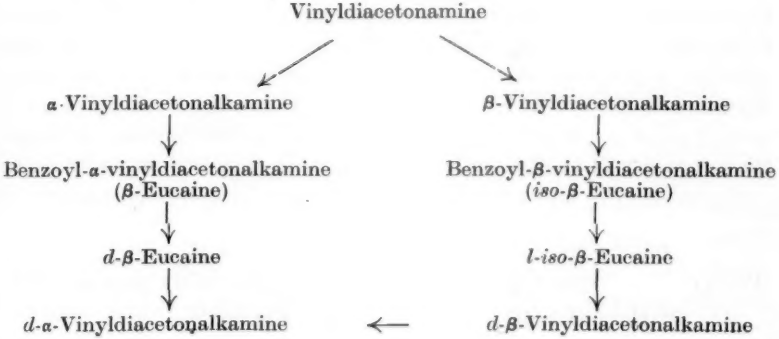
The chemical results with *iso*-β-eucaine are tabulated below :

	l-iso-β-Eucaine.	*d-iso-β*-Eucaine.	*dl-iso-β*-Eucaine.
Base :			
Appearance	Syrup	Syrup	Syrup
Hydrochloride :			
Appearance	Bold needles	Bold needles	Dimorphous, needles and plates
M. p.	271—273° corr.	271—273° corr.	269—271° corr.
$[\alpha]_{5461}$	−16·3°	+17·0°	—
Picrate :			
Appearance	Needles	—	Rectangular leaflets
M. p.	280° corr.	—	256—258° corr.

Tutin (T., 1910, **97**, 1797) has directed attention to the unusual fact for a picrate that benzoyl-*d*-oscine picrate melts at 211—212° without decomposition. A still more striking example is furnished by *dl-iso*-β-eucaine picrate, which melts at 256—258° without decomposition and if the melting point tube be removed from the bath its contents resolidify and will melt again at the original temperature.

As β-vinyldiacetonalkamine is, according to Harries, converted *quantitatively* into α-vinyldiacetonalkamine by boiling with sodium amyloxide, the behaviour of the optically active forms to the same reagent was deemed worthy of investigation. Accordingly, *l-iso*-β-eucaine was hydrolysed, giving d-β-*vinyldiacetonalkamine*, which on boiling with sodium amyloxide for thirty-two hours gave a 77 per cent. yield of d-α-*vinyldiacetonalkamine hydrochloride* having $[\alpha]_{5461} + 17{\cdot}6°$, whereas the pure salt has $[\alpha]_{5461} + 18{\cdot}5°$. The racemising influence of the sodium amyloxide is thus confined to the >CH·OH group and does not involve the other asymmetric centre.

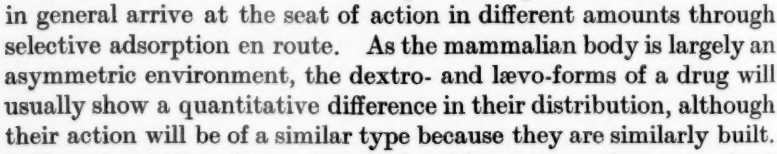
The vinyldiacetonalkamines, *racemic* and *active*, have been fully characterised as *bases*, and by preparation of their *hydrochlorides* and *picrates*. The circuit of reactions detailed in this communication is summarised by the following diagram :



The author is much indebted to Dr. J. H. Burn of these laboratories for a determination of the relative anæsthetic action of β-eucaine, *iso*-β-eucaine, and their optically active forms. On the rabbit's cornea β-eucaine, *iso*-β-eucaine, and their optically active components have approximately equal local anæsthetic action, the limiting concentration for complete anæsthesia lying between 0·25 and 0·5 per cent. On the sciatic nerve of the frog, however, β-eucaine is a more potent anæsthetic than *iso*-β-eucaine; *d*- and *l*-β-eucaines in 5 per cent. solution completely block the impulses produced by electrical stimuli applied to the nerve in fifteen to twenty minutes, their effectiveness being approximately equal; but *d*- and *l*-*iso*-β-eucaines in 5 per cent. solution have little effect in blocking the impulses even after twenty minutes.

How do these results fall in with the general trend of observations on the relation between physiological action and chemical constitution? Although the fundamental chemical mechanism of the action of drugs is not known with any certainty, the present position may be very broadly summarised by the statement that the physiological action which results from the application of a drug is mainly a matter of its distribution in the tissues. The classic work of Dale and Barger on the adrenaline-like action of derivatives of ethylamine shows that a great number of substances of this type exist which have a similar action, but differ in the quantitative aspect. It seems that the same physiological receptor or receptors are concerned in each case, but the amount of drug which arrives at the seat of action differs in each case. Similarity of chemical build thus determines similarity of localisation and resultant physiological action. The reason, however, for the difference in the quantitative aspect of the phenomena is suggested by the recent remarkable observations of Porter and Ihrig (*J. Amer. Chem. Soc.*, 1923, **45**, 1990), who showed that wool treated with racemic *m*-azo-β-naphtholmandelic acid has a selective affinity for the *dextro*-form, the unused dye being almost a pure *lævo*-form. It seems likely that two substances of similar build, on penetrating tissues, will therefore in general arrive at the seat of action in different amounts through selective adsorption en route. As the mammalian body is largely an asymmetric environment, the dextro- and lævo-forms of a drug will usually show a quantitative difference in their distribution, although their action will be of a similar type because they are similarly built.

Hyoscine (IV) and atropine (V) furnish an interesting example of



such relationship. Their similarity in build is plain and part of the physiological picture of the action of hyoscine is made up of atropine-like effects. Working with the *d*- and *l*-hyoscines prepared by the author (T., 1919, **115**, 476), Cushny found (*J. Pharm. Exp. Ther.*, 1921, **17**, 41) that *l*-hyoscine is 15 to 18 times as powerful as *d*-hyoscine in its specific atropine effects, but on nerve endings in striated muscle, on unstriated muscle, and on the central nervous system their action is identical.

The relative anæsthetic actions of β- and *iso*-β-eucaines may be interpreted in analogous terms. β- and *iso*-β-Eucaines and their optically active forms are all equally anæsthetic on the cornea; they are similarly built and similarly localised, and any quantitative difference in their intensity of action is not measurable by present methods. On the sciatic nerve of the frog, β-eucaine is more potent than *iso*-β-eucaine and the action of *d*- and *l*-β-eucaine is equal; here again the action of β- and *iso*-β-eucaines is of the same type, but there is a quantitative difference indicating a difference of penetrating power.

The toxicity of these bases was determined on mice by subcutaneous injection and is expressed in milligrams per gram of mouse :

r-β-Eucaine	0·8—0·9	*r-iso*-β-Eucaine	0·5
d-β-Eucaine	1·5	*d-iso*-β-Eucaine	0·5
l-β-Eucaine	0·6—0·7	*l-iso*-β-Eucaine	0·5

As *d*- and *l*-β-eucaines are equally anæsthetic and *l*-β- is about twice as toxic as *d*-β-eucaine, if other factors were equal, the use of *d*-β-eucaine would be indicated in preference to *l*- or *r*-β-eucaine.

Experimental.

Preparation of α- and β-Vinyldiacetonalkamines.

For the preparation of these bases Harries's method (*Annalen*, 1897, **294**, 336) was in the main followed. The separation of the two hydrochlorides by reason of the sparing solubility of the α-vinyldiacetonalkamine hydrochloride in a mixture of equal volumes of alcohol and ether is not quantitative and the addition of the ether can be omitted without disadvantage. After isolation of as much α- and β-bases as possible by a repetition of the above process on the contents of the mother-liquors, there always remains an uncrystallisable residue in the benzene mother-liquors of the β-base. This was fractionated by distillation under reduced pressure at 20 mm. Between 120° and 130° (external bath temperature), a limpid oil distilled over and consisted of unreduced vinyldiacetonamine. Between 140° and 150° a mixture of α- and β-vinyldiacetonalkamines came over and rapidly solidified, and finally between 180° and 200° a viscous liquid distilled, the latter portions

of which readily crystallised. This high-boiling fraction is in all probability the pinacol formed by fusion of the two nuclei. As it was a mixture and probably consisted of six possible forms, two meso and four racemic, it was not further investigated. It appears to be formed to the extent of between 5 and 10 per cent. during the ordinary process of reduction by sodium amalgam.

α-*Vinyldiacetonalkamine picrate*, prepared from the free base, is very readily soluble in water and crystallises in well-formed, orange prisms, m. p. 238—239° (corr.).

β-*Vinyldiacetonalkamine picrate* is even more soluble than the picrate of the α-base. For its preparation the free base must be used and excess of picric acid avoided. It crystallises from water in laminæ formed by the fusion of needles, m. p. 171—172° (corr.).

Vinyldiacetonamine picrate, prepared from its components, is soluble to the extent of 1 part in 57 parts of boiling water and crystallises in clusters of prisms, m. p. 198—199° (corr.; decomp.).

β-*Eucaine and Optically Active Acids.**

Camphoric Acid.—β-Eucaine (1·0 gram) was mixed with a one-half molecular proportion (0·4 gram) of *d*-camphoric acid and dissolved in boiling methyl ethyl ketone. The crystalline β-eucaine camphorate was recrystallised thrice from methyl ethyl ketone. The melting point was unchanged throughout and β-eucaine regenerated from the final salt was devoid of optical activity.

dl-β-*Eucaine* d-*camphorate* crystallises from methyl ethyl ketone in very compact clusters of plates, m. p. 211—212° (corr.). It is readily soluble in the boiling solvent but sparingly soluble in the cold (Found : C = 68·9; H = 8·4. $C_{10}H_{16}O_4,2C_{15}H_{21}O_2N$ requires C = 69·1; H = 8·4 per cent.).

l-*Malic Acid.*—β-Eucaine (4·94 grams) was mixed with one molecular proportion (2·68 grams) of *l*-malic acid in aqueous solution, but the salt which separated was the normal salt (3·45 grams), having $[\alpha]_D$ — 2·6° in water. It was recrystallised twice more from water, yielding 1·85 grams of salt with properties unchanged. A quantity (1·4 grams) was decomposed with dilute ammonia and the recovered β-eucaine proved to be optically inactive in hydrochloric acid solution.

dl-β-*Eucaine* l-*malate* crystallises readily from water. It is anhydrous and melts at 212—213° (corr.) (Found : C = 64·8;

* A sample of β-eucaine of unknown origin crystallised with bromocamphorsulphonic acid from alcohol gave an extremely insoluble salt, m. p. 283—284° (corr.) (Found : C = 54·1; H = 6·6. Calc., C = 53·7; H = 6·5 per cent.). It gave a syrupy base and a lævorotatory, crystalline hydrochloride, not identical, however, with *l*-β-eucaine or *l*-*iso*-β-eucaine.

H = 7·6. $C_4H_6O_5,2C_{15}H_{21}O_2N$ requires C = 64·9; H = 7·7 per cent.). The specific rotation was determined in water: $c = 1·06$; $l = 2$ dcm.; α_D − 0·05°; $[\alpha]_D$ − 2·6°, whence $[M]_D$ for the normal malate-ion is −16·3°. This is of the same order as the value −17·2° obtained by extrapolation from Schneider's values (*Annalen*, 1881, **207**, 271) for sodium malate.

d-*Tartaric Acid.*—Equimolecular proportions of β-eucaine (4·9 grams) and *d*-tartaric acid (3·0 grams) were dissolved in water. The salt which separated was, however, the normal salt (yield 2·2 grams), reacting neutral to litmus. On addition of a second molecular proportion of β-eucaine to the mother-liquors a large crop (5·9 grams) of the normal salt was obtained having $[\alpha]_D$ + 9·6°. The rotations after two more crystallisations were + 11·2° and 10·1°, respectively. There was no evidence of resolution.

dl-β-*Eucaine* d-*tartrate* crystallises from water without solvent of crystallisation, in large tablets which melt and decompose at 257° (corr.) (Found: C = 63·4; H = 7·5. $C_4H_6O_6,2C_{15}H_{21}O_2N$ requires C = 63·3; H = 7·5 per cent.). The specific rotation was determined in water: $c = 0·53$; $l = 2$ dcm.; α_D + 0·11°; $[\alpha]_D$ + 10·1°.

β-*Eucaine and* d-*Camphor*-10-*sulphonic Acid.*

Crystallisation without Resolution.—4·9 Grams of β-eucaine were combined in alcoholic solution with one equivalent (5·2 grams) of *d*-camphor-10-sulphonic acid. On keeping at room temperature or at zero, *dl*-β-eucaine *d*-camphor-10-sulphonate separated in massive tablets. The yield was 7·5 grams and the specific rotation $[\alpha]_D$ + 10·7°. On recrystallisation it separated in two forms, needles and tablets, but on keeping over-night the needles had disappeared, leaving the more stable form of tablets. The sequence of rotation for the successive crystallisations of the stable tablet form was $[\alpha]_D$ + 10·7°, 8·2°, 9·4°, 10·4°, mean 9·69°, whence for the salt deprived of solvent of crystallisation, $[\alpha]_D$ + 10·6° in agreement with the value 10·6° calculated from Graham's value (T., 1912, **101**, 747) for the camphorsulphonic-ion. There was no resolution of the β-eucaine.

dl-β-*Eucaine* d-*camphor*-10-*sulphonate* crystallises from alcohol in large tablets containing one molecule of alcohol of crystallisation, which is lost gradually on exposure to the air (Found: loss at 100° = 8·7. $C_{15}H_{21}O_2N,C_{10}H_{16}O_4S,C_2H_5·OH$ requires loss = 8·8 per cent.). This salt is weakly triboluminescent and melts at 228—229° (corr.). Its specific rotation was determined in water: $c = 1·02$; $l = 2$ dcm.; α_D + 0·19°; $[\alpha]_D$ + 9·37°, whence for salt without solvent of crystallisation $[\alpha]_D$ + 10·3°.

Crystallisation with Resolution.—29·7 Grams of β-eucaine were neutralised with 31·2 grams of *d*-camphor-10-sulphonic acid in alcoholic solution. A large crop of leaflets was obtained weighing 55·9 grams, melting at 223—225°, and having $[\alpha]_D$ + 9·85° in water. On recrystallisation, this commenced to crystallise in leaflets, but on keeping over-night partial transformation into massive tablets had taken place and after another twenty-four hours transformation was complete. This salt proved to be the partial racemate described in the foregoing section. It weighed 52 grams, melted at 225°, and had $[\alpha]_D$ + 9·3° in water. It was recrystallised from alcohol, the leaflet form of crystal separating first. By exercising care and patience it was found possible to carry out the successive recrystallisations in the absence of the partial racemate, but once the tablets of the partial racemate appeared, as frequently happened when the crystallisation was allowed to proceed over-night, solution of the less stable, partially resolved phase rapidly followed. When, however, the resolution was nearly complete this no longer occurred, as the solubility limit of the partial racemate could no longer be attained. After seven crystallisations, *l*-β-eucaine *d*-camphor-10-sulphonate (8·6 grams) was obtained pure. By working through the mother-liquors a further 7·8 grams were obtained pure, representing a total yield of 54 per cent.

l-β-*Eucaine* d-*camphor*-10-*sulphonate* crystallises in rectangular leaflets, m. p. 248—249° (corr.) (Found : C = 62·9; H = 7·9. $C_{15}H_{21}O_2N,C_{10}H_{16}O_4S$ requires C = 62·6; H = 7·8 per cent.). The specific rotation was determined in water; *c* = 1·04; *l* = 2 dcm.; α_D + 0·10°, 0·10°; $[\alpha]_D$ + 4·78°, + 4·83°, whence it is calculated for the *l*-β-eucainium-ion, $[\alpha]_D$ − 11·0°. Another preparation gave $[\alpha]_{5461}$ + 7·3°, whence for the *l*-β-eucainium-ion $[\alpha]_{5461}$ − 12·7°.

It was not found possible to isolate *d*-β-eucaine *d*-camphor-10-sulphonate from the mother-liquors, as the two salts *d*-β-eucaine *d*-camphorsulphonate and *l*-β-eucaine *d*-camphorsulphonate form a continuous series of mixed crystals. The isolation of the *d*-β-eucaine salt was rendered feasible as follows : After removal of 6 grams of partially resolved salt, the solution was crystallised as the partial racemate. Seventeen grams of this salt were obtained and from the final combined mother-liquors, now rich in *d*-β-eucaine *d*-camphorsulphonate, the base was recovered, and neutralised with *l*-camphor-10-sulphonic acid. *d*-β-Eucaine *l*-camphorsulphonate crystallised readily and after three crystallisations was pure. The yield was 10·2 grams, or 34 per cent. of that possible.

d-β-*Eucaine* l-*camphor*-10-*sulphonate* was identical in its gross properties with *l*-β-eucaine *d*-camphor-10-sulphonate described above. Its rotation was determined in water : *c* = 1·01; *l* = 2

dcm.; $\alpha_D - 0{\cdot}1°$; $[\alpha]_D - 5{\cdot}09°$, whence it is calculated for the *d*-β-eucainium-ion, $[\alpha]_D + 10{\cdot}6°$.

dl-β-*Eucaine* dl-*camphor*-10-*sulphonic acid* was prepared from its components in alcoholic solution. It crystallised at first in very fine needles, but on keeping these disappeared and were replaced by six-sided plates. It also crystallises in rectangular plates. It melts at 217—219° (corr.) (Found : C = 62·7; H = 7·8.

$$C_{15}H_{21}O_2N,C_{10}H_{16}O_4S$$

requires C = 62·6; H = 7·8 per cent.).

The Active Eucaines and Salts.

l-β-*Eucaine Base.*—7·5 Grams of *l*-β-eucaine *d*-camphorsulphonate were decomposed by the aid of dilute ammonia and the free base was taken up in ether. On removal of the ether the free base crystallised readily and was obtained quite pure by crystallisation from low-boiling petroleum (40—60°). It crystallises in large prisms or columns and melts at 57—58° (corr.). It is more readily soluble in petroleum than *r*-β-eucaine base.

l-β-*Eucaine Hydrochloride.*—This salt was prepared from the base by neutralisation with hydrochloric acid. It crystallises readily in large, rectangular plates with some of the corners bevelled and is more soluble than *r*-β-eucaine hydrochloride. It melts at 244—245° (corr.). The specific rotation was determined in water : $c = 1{\cdot}21$; $l = 2$ dcm.; $\alpha_D - 0{\cdot}27°$; $[\alpha]_D - 11{\cdot}3°$, whence for the *l*-β-eucainium-ion $[\alpha]_D - 13{\cdot}0°$, as compared with the value $[\alpha]_D - 11{\cdot}0°$ calculated from the *d*-camphorsulphonate. Another preparation of the hydrochloride gave $[\alpha]_{5461} - 12{\cdot}4°$, whence for the ion $[\alpha]_{5461} - 14{\cdot}2°$.

l-β-*Eucaine Picrate.*—This salt, prepared from the base and saturated picric acid solution, is very sparingly soluble even in boiling water. It is conveniently recrystallised from spirit and separates in fan-shaped clusters of small prisms, m. p. 198—199° (corr.), without decomposition.

d-β-*Eucaine Base.*—Prepared similarly to the lævo-base, this melts at 57—58° (corr.) and crystallises from low-boiling petroleum in large columns.

d-β-*Eucaine hydrochloride* was identical in its gross properties with *l*-β-eucaine hydrochloride. Its specific rotation was determined in water : $c = 1{\cdot}21$; $l = 2$ dcm.; $\alpha_D + 0{\cdot}28°$; $[\alpha]_D + 11{\cdot}5°$, whence for the *d*-β-eucainium-ion $[\alpha]_D + 13{\cdot}1°$, as compared with the value $[\alpha]_D + 10{\cdot}6°$ calculated from the *l*-camphorsulphonate.

Racemic Eucaine and its Salts.

r-β-*Eucaine Hydrochloride.*—Equal weights of *d*- and *l*-β-eucaine hydrochlorides were dissolved in water. The relatively sparingly soluble *r*-β-eucaine hydrochloride separated readily in small tablets which were almost rectangular and often possessed an opaque appearance. It melts at 277—279° (corr.) without decomposition, either in an open or sealed capillary. A relatively large proportion of *d*-β-eucaine hydrochloride mixed with a small proportion of *r*-β-eucaine hydrochloride shows a depression of melting point of about 4°.

r-β-*Eucaine base,* prepared from the pure *r*-β-eucaine hydrochloride, crystallises well from low-boiling petroleum in large diamond- or hexagonal-shaped plates, m. p. 70—71° (corr.). A small quantity mixed with a preponderating quantity of the dextro-base melted at 53° (corr.), whereas the *d*-base melted simultaneously at 60°. *r*-β-Eucaine base is therefore a true racemate, unless indeed the melting-point curve shows a discontinuity where the racemic base phase passes into a pseudo-racemic.

r-β-*Eucaine picrate,* prepared from the pure racemic base in alcoholic solution, is very sparingly soluble in boiling alcohol and crystallises in diamond-shaped plates, m. p. 230·5—231·5° (corr.) (Gadamer, " Lehrbuch der chem. Toxicol.," gives 230°).

Hydrolysis of d-β-*Eucaine.*

Two grams *d*-β-eucaine hydrochloride were boiled for an hour with 20 c.c. of 15 per cent. hydrochloric acid, when the reaction with Mayer's reagent was negative. After removal of benzoic acid the acid liquors were concentrated to a small volume, when the hydrochloride of the required base crystallised readily.

d-α-*Vinyldiacetonalkamine hydrochloride* crystallises readily from water in many-faced tablets which are anhydrous. It is unmelted at 300°. Its rotation was taken in water: $c = 1{\cdot}2$; $l = 2$; $\alpha_D + 0{\cdot}32°$; $[\alpha]_D + 13{\cdot}3°$, whence for the *d*-α-vinyldiacetonalkammonium-ion $[\alpha]_D + 16{\cdot}5°$.

In a similar manner l-α-*vinyldiacetonalkamine hydrochloride* was prepared by hydrolysis of *l*-β-eucaine. It was unmelted at 300°. Its rotation was determined in water: $c = 1{\cdot}22$; $l = 2$; $\alpha - 0{\cdot}45°$; $[\alpha]_{5461} - 18{\cdot}5°$, whence for the *l*-α-vinyldiacetonalkammonium-ion $[\alpha]_{5461} - 23{\cdot}1°$.

l-α-*Vinyldiacetonalkamine base* is liberated as an oil, which soon solidifies, on making the solution of its hydrochloride strongly alkaline (about 33 per cent. sodium hydroxide) by addition of solid sodium hydroxide. Crystallised from benzene, it separates in large

prisms, often 1 cm. long and 0·4 mm. wide, melting at 79—81° (corr.). A mixture with a small proportion of *dl*-α-vinyldiacetonalkamine melted definitely lower by about 2°.

l-α-*Vinyldiacetonalkamine picrate*, prepared from exact molecular proportions of its components, is very readily soluble in water. It separates on concentration in fine needles, m. p. 242—244° (corr.).

Preparation of N- *and* O-*Benzoyl*-β-*vinyldiacetonalkamines.*

(a) *From* β-*Vinyldiacetonalkamine Base.*—The finely powdered β-base (2·35 grams) was treated with 2·6 grams of benzoyl chloride. On keeping for a few minutes, a vigorous reaction took place with solution of the crystals. The product was now examined without further heating. Ethereal extraction of the acid aqueous solution gave, after removal of benzoic acid by dilute alkali, 1·2 grams of crude N-*benzoyl* β-*vinyldiacetonalkamine*. It was crystallised from benzene and separated in filmy leaflets melting at 121—122° (corr.).

The acid aqueous liquors, made alkaline with ammonia and extracted with ether, gave a 35 per cent. yield of *O*-benzoyl-β-vinyldiacetonalkamine and on making strongly alkaline (equivalent to 33 per cent. sodium hydroxide) gave 0·9 gram of unchanged β-vinyldiacetonalkamine.

(b) *From* β-*Vinyldiacetonalkamine Hydrochloride.*—Pure β-vinyldiacetonalkamine (14·3 grams) was neutralised with *N*-hydrochloric acid and evaporated dry under reduced pressure with repeated addition of absolute alcohol. After removal of solvent as completely as possible, the residual syrup often crystallised throughout. The reaction with benzoyl chloride proceeded more smoothly with the syrupy salt than the crystalline. Benzoyl chloride (13 c.c.) was added and the mixture heated at 150° for two hours. The vinyldiacetonalkamine hydrochloride gradually passed into solution, if crystalline, and the whole contents set to a crystalline magma of *O*-benzoyl-β-vinyldiacetonalkamine hydrochloride. The product is best recrystallised direct from water after extraction with ether, which removes benzoic acid, a little ethyl benzoate, but no *N*-benzoyl derivatives. The yield of pure *O*-benzoyl-β-vinyldiacetonalkamine hydrochloride is 90 per cent. of the theoretical.

O-*Benzoyl*-β-*vinyldiacetonalkamine* (iso-β-*eucaine hydrochloride*) crystallises from double its weight of hot water either in silky needles or in diamond-shaped plates. Both forms are anhydrous and the latter is the more stable, conversion of the needle form into the plate form taking place on seeding with the plate form. The appearance of the needle form in solutions of the pure salt is fortuitous, but in working up the mother-liquors of the benzoylation this form appears more frequently. Both forms melt at 269—271°

(corr.) (Found : C = 63·4; H = 7·9. $C_{15}H_{21}O_2N$,HCl requires C = 63·5; H = 7·8 per cent.).

O-*Benzoyl*-β-*vinyldiacetonalkamine picrate*, prepared from the hydrochloride, is sparingly soluble in boiling water. Crystallised from diluted alcohol, it separates in delicate, rectangular leaflets with bevelled corners. It melts without decomposition at 256—258° (corr.).

The free *base* is a syrup showing no signs of crystallisation when kept for twenty-four hours at — 5°.

Resolution of iso-β-*Eucaine.*

(a) *With* d-*camphor*-10-*sulphonic acid* an extremely readily soluble salt was formed which could not be crystallised.

(b) *With* d-α-*Bromo*-π-*camphorsulphonate.* — *Experiment A.* Twenty-six grams of *iso*-β-eucaine *d*-α-bromo-π-camphorsulphonate were fractionally crystallised from absolute alcohol, the successive crops showing rapidly increasing rotations, the fourth, amounting to 2·8 grams, having $[\alpha]_{5461}$ + 66°, whereas pure d-*iso*-β-eucaine *d*-α-bromo-π-camphorsulphonate has $[\alpha]_{5461}$ 68·5°. As considerable difficulties were encountered in effecting further separation of the contents of the mother-liquors, it was decided to prepare a much larger batch.

Experiment B. *iso*-β-Eucaine *d*-bromocamphorsulphonate (104 grams) was fractionally crystallised from absolute alcohol. The first crop, 74·5 grams, had $[\alpha]_{5461}$ + 59·3° and after six more crystallisations gave pure *l-iso*-β-eucaine *d*-bromocamphorsulphonate (11·2 grams) having $[\alpha]_{5461}$ + 52·3°. On working through the mother-liquors once, 11·85 grams of *d-iso*-β-eucaine *d*-bromocamphorsulphonate, having $[\alpha]_{5461}$ + 68·3°, were obtained. On working through a second time, 6·95 grams of *d-iso*-β-eucaine *d*-bromocamphorsulphonate, having $[\alpha]_{5461}$ + 68·8°, were obtained. Repeating the process a third time, 17·25 grams of *l-iso*-β-eucaine *d*-bromocamphorsulphonate, having $[\alpha]_{5461}$ + 52·0°, were obtained and finally 7·4 grams of *d-iso*-β-eucaine *d*-bromo-π-camphorsulphonate, having $[\alpha]_{5461}$ + 68·6°. The yield of pure *l-iso*-β-eucaine *d*-bromocamphorsulphonate was thus 55 per cent. and that of *d-iso*-β-eucaine *d*-bromocamphorsulphonate 45 per cent. of that possible.

l-iso-β-*Eucaine* d-α-*bromo*-π-*camphorsulphonate* crystallises from three parts of boiling alcohol in microscopic needles. It also crystallises from water in glistening, silky needles. It melts at 236—238° (corr.). Its rotation was determined in water, two different preparations giving the following results :

$c = 0{\cdot}80$; $l = 2$; α + 0·84°; $[\alpha]_{5461}$ + 52·26°
$c = 0{\cdot}81$; $l = 2$; α + 0·84°; $[\alpha]_{5461}$ + 51·96°,

whence mean value $[\alpha]_{5461}$ + 52·1° and $[M]_{5461}$ + 290·9°. Using the value $[M]_{5461}$ + 346·5° given by Pope and Read (T., 1910, **97**, 2200) for the *d*-bromocamphorsulphonic-ion, it is calculated that $[M]_{5461}$ for the *l-iso*-β-eucainium-ion is − 55·6° and $[\alpha]_{5461}$ − 22·4°. The salt is anhydrous (Found : C = 54·2; H = 6·5.

$$C_{15}H_{21}O_2N,C_{10}H_{15}O_4BrS$$

requires C = 53·7; H = 6·5 per cent.).

d-iso-β-*Eucaine* d-α-*bromo-π-camphorsulphonate* crystallises from alcohol in minute needles. It dissolves in two parts of boiling alcohol and the air-dried salt contains between one-half and one molecule of water of crystallisation (Found : on various preparations, loss at 100° = 1·65, 2·5, 2·1; on anhydrous salt, C = 53·5; H = 6·7. $C_{15}H_{21}O_2N,C_{10}H_{15}O_4BrS$ requires C = 53·7; H = 6·5; $3/4H_2O$ = 2·4 per cent.).

Its rotation was determined in water, three different preparations giving the following values for the air-dried salts :

$c = 0{\cdot}81$; $l = 2$; α + 1·11°; $[\alpha]_{5461}$ + 68·3°
$c = 0{\cdot}80$; $l = 2$; α + 1·11°; $[\alpha]_{5461}$ + 68·8°
$c = 0{\cdot}80$; $l = 2$; α + 1·10°; $[\alpha]_{5461}$ + 68·6°

Correcting for the water content of each and taking the mean gives $[\alpha]_{5461}$ + 70·0° for the anhydrous salt, whence $[M]_{5461}$ + 391° and from this it may be calculated for the *d-iso*-β-eucainium-ion $[\alpha]_{5461}$ + 17·8°.

d-iso-β-*Eucaine Hydrochloride*.—The free base was liberated from the bromocamphorsulphonate by ammonia, extracted with ether, and obtained as an uncrystallisable syrup. It was converted into the hydrochloride, which crystallised extremely well from water in bold, glistening needles. It melts at 271—273° (corr.) and is anhydrous. Its rotation was determined in water : $c = 1{\cdot}00$; $l = 2$; α + 0·3°; $[\alpha]_{5461}$ + 14·9°, whence for the *d-iso*-β-eucainium-ion $[\alpha]_{5461}$ + 17·0°. This compares favourably with the value + 17·8° calculated above from the rotation of the bromocamphorsulphonate.

l-iso-β-*Eucaine Hydrochloride*.—This salt melted at 271—273° (corr.). Its rotation was determined in water : $c = 1{\cdot}0$; $l = 2$; α − 0·28°; $[\alpha]_{5461}$ − 14·25°, whence for the *l-iso*-β-eucainium-ion $[\alpha]_{5461}$ − 16·3°, a value close to that of the *d*-salt but showing considerable variation from that, − 22·4°, calculated from the bromocamphorsulphonate.

l-iso-β-*Eucaine Picrate*.—This salt is very sparingly soluble in boiling water. It separates from diluted alcohol in fine needles and melts at 280° (corr.).

Hydrolysis of l-iso-β-*Eucaine.*

l-iso-β-Eucaine hydrochloride (10 grams) was boiled for three hours with 15 per cent. hydrochloric acid, when the reaction with Mayer's reagent was negative. After removal of benzoic acid, the solution was evaporated to dryness under reduced pressure with addition of alcohol and the residue crystallised from a mixture of absolute alcohol and dry ether.

d-β-*Vinyldiacetonalkamine hydrochloride* crystallises in tablets and melts at 217—219° (corr.). Its rotation was determined in water; $c = 1{\cdot}34$; $l = 2$; $\alpha + 0{\cdot}61°$; $[\alpha]_{5461} + 22{\cdot}85°$, whence for the *d*-β-vinyldiacetonalkammonium-ion $[\alpha]_{5461} + 28{\cdot}5°$.

d-β-*Vinyldiacetonalkamine* was prepared by addition of 3 grams of sodium hydroxide to a solution of 5·3 grams of the hydrochloride dissolved in 10 c.c. of water. The free base separated in six-sided plates. It was recrystallised from benzene and separated in well-formed tablets melting at 121—123° (corr.).

d-β-*Vinyldiacetonalkamine picrate*, prepared from exact molecular equivalents of the components, is extremely soluble in boiling water, but much less soluble in cold. It crystallises in fine, radiating needles and melts at 181—182° (corr.).

Action of Sodium Amyloxide on d-β-*Vinyldiacetonalkamine.*

d-β-Vinyldiacetonalkamine (3·6 grams) was boiled for thirty-two hours with 7·5 grams of sodium dissolved in 75 c.c. of amyl alcohol (b. p. 130°). The solution was steam-distilled so long as any alkaline-reacting material passed over. The distillate was acidified with hydrochloric acid, the amyl alcohol removed by a separator and finally by ether, and the solution evaporated to dryness under reduced pressure with addition of alcohol. The product was digested with 10 c.c. of absolute alcohol and filtered after standing for a few hours. The alcohol-soluble fraction amounted to 0·9 gram and the alcohol-insoluble to 2·95 grams. The latter was unmelted at 300° and had $[\alpha]_{5461} + 17{\cdot}6°$ in water ($c = 1{\cdot}2$). As the rotation of pure *d*-α-vinyldiacetonalkamine hydrochloride is $[\alpha]_{5461} + 18{\cdot}5°$, the product was almost pure *d*-α-vinyldiacetonalkamine hydrochloride; a mixture containing 2·4 per cent. of the *l*-salt would give $[\alpha]_{5461} + 17{\cdot}6°$. To confirm its identity, 2·5 grams were converted into the free base and crystallised from benzene. It separated in perfectly formed, long prisms of hexagonal outline and melted at 79—81° (corr.), as did the pure *l*-base in the same bath.

Preparation of ON-*Dibenzoyl-α- and -β-vinyldiacetonalkamines.*

ON-*Dibenzoyl-α-vinyldiacetonalkamine* was prepared by heating β-eucaine base (3·6 grams) with benzoic anhydride (1 mol.) at 160°

for two hours. The crude, non-basic portion containing the dibenzoyl derivative amounted to 1·7 grams. It was deeply pigmented, but crystallised readily. It was best recrystallised from alcohol and separated in six-sided plates, m. p. 142—143° (corr.). From the basic portion of the liquors 3·0 grams of β-eucaine hydrochloride were recovered (Found : C = 75·1 ; H = 7·2. $C_{22}H_{25}O_3N$ requires C = 75·2 ; H = 7·2 per cent.).

ON-*Dibenzoyl*-β-*vinyldiacetonalkamine* was prepared in a similar manner from *iso*-β-eucaine base. It crystallises best from ether, separating in flattened prisms, m. p. 114—115° (corr.).

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VIII.—*The Rapid Admixture of Hot Combustible Gases with Air.*

By Frank Maurice Cray and William Edward Garner.

Mixtures of combustible gases and air, after attaining the ignition temperature, pass through a rapidly accelerating process of combustion, which finally culminates in the appearance of flame. The interval of time which elapses between the attainment of the normal ignition temperature and the commencement of ignition is known as the pre-flame period, and the duration of this period depends on the temperature coefficient of the combustion process and on the magnitude of the thermal changes accompanying the chemical reactions. The pre-flame period for a few gaseous mixtures has been studied by several investigators. Dixon, Bradshaw, and Campbell (T., 1914, **105**, 2027) have shown that the period of pre-flame for a mixture of hydrogen and oxygen, when heated by compression, is of the order of 1/100 of a second, and recently, Tizard and Pye (*Phil. Mag.*, 1922, [vi], **44**, 79) have determined the delay in ignition which occurs when mixtures of heptane, ether, or carbon disulphide with air are ignited in the same manner. From the latter investigation, it appears that delays of the order of one second may occur when a gaseous mixture is heated just above its ignition temperature, but that the delay decreases with increasing temperature; at temperatures 50° above the ignition temperature, the delay is very small though still appreciable. Also Will (*Z. ges. Schiess- u. Sprengstoffw.*, 1909, **4**, 302, 323, 343) has observed the occurrence of a period of pre-flame when the gaseous products from the detonation of high explosives were rapidly projected into

cold air. In the case of several explosives containing insufficient oxygen for complete self-combustion, ignition did not occur immediately after admixture of the combustible gases with the surrounding air, and photographs of the explosion showed two distinct emissions of light, one due to the hot unignited gases, and the other, after an interval of time, due to their secondary combustion in the air. The duration of the interval between the two flashes was 2—6-thousandths of a second for explosions of picric acid and trinitrotoluene. In these circumstances, the occurrence of ignition is dependent, not only on the temperature of the hot gases and on the time of pre-flame, but also on the rapidity of admixture of the hot gases with the cold air. In some of Will's experiments with trinitrotoluene the second flash was not observed, and in these cases it appears that the hot combustible gases were mixed so rapidly with the surrounding air that they were chilled below their normal ignition temperature within the time of pre-flame.

The factors which determine the " after-ignition " of the gases from the explosive processes are so complex that it is not easy to devise a promising line of attack on the problem. In the present paper, two attempts have been made to study the behaviour of hot gases on admixture with air, and although their original purpose has not been achieved, it is thought that the results obtained are of sufficient interest to warrant their publication, especially as there is little likelihood of our continuing the investigation in the near future. In the first series of experiments, the source of the hot combustible gases was picric acid contained in small steel containers, and in the second, acetylene and oxygen mixtures contained in thin glass bulbs.

Part I. Detonation of Picric Acid in Steel Containers.

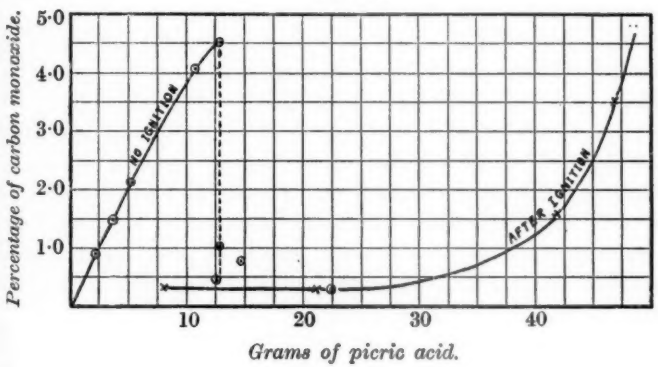
The object of these experiments was to investigate the effect of variations in the ratio of the volume of the explosive gases to the volume of the air into which they were projected, the other conditions, for example, the work done on the container per gram of explosive, the density of the explosive, etc., being kept as uniform as possible. With this end in view, the explosive was contained in cylindrical steel containers, drilled out of solid steel, with an internal diameter of 0·4 inch, and with walls and base 0·25 inch thick, and fired under standard conditions by a lead azide detonator, in a large closed vessel of 86·7 litres capacity, in an atmosphere of air. This volume of air gives sufficient oxygen for the complete combustion of approximately 55 grams of picric acid, and, on this account, the amounts of explosive were not allowed to exceed 50 grams. The length of the container and the weights of the

explosives were the only variables in these experiments. The density of the picric acid, which was in the form of pellets, was 1·30 throughout.

In addition, a few detonations were carried out in containers with an internal diameter of 1 inch and with a wall thickness of 0·25 inch. It was hoped that the results of these experiments would throw light on the part played by the cooling of the gases due to the work done on the container. The cooling due to this cause should not be so great in this as in the first series, for the amount of explosive operating on a sq. cm. of steel surface is much greater.

To obtain a measure of the combustion, the volume of carbon monoxide in the residual gases was determined and compared with

FIG. 1.



that found when the explosive was detonated under similar conditions in a vacuum. The carbon monoxide was analysed by the iodine pentoxide method. The results which were obtained are given in Tables I and II, and are summarised in the curve (Fig. 1).

TABLE I.

Containers 0·4 inch internal diameter.

No. of expt.	Picric acid (grams).	Per cent. CO.	Vol. of CO (c.c./ gram).	No. of expt.	Picric acid (grams).	Per cent. CO.	Vol. of CO (c.c./ gram).
1	2·145	0·87	334	6	12·64	5·70	410
2	3·67	1·48	338	7	12·84	1·01	72
3	5·2	2·12	346	8	12·86	4·49	317
4	10·84	4·05	332	9	14·65	0·76	46
5	12·48	0·44	32	10	22·35	0·28	11

Volume of CO from explosion in a vacuum = 323 c.c./gram.

TABLE II.

Containers 1·0 *inch internal diameter.*

No. of expt.	1	2	3	4
Picric acid (grams)	8·0	21·04	41·59	46·77
Per cent. CO	0·3	0·26	1·58	3·76

When weights of picric acid ranging from 2 to 12 grams were taken in the containers (0·4 inch in diameter), the volume of carbon monoxide per gram of explosive (column 4) in the final gases agreed with that obtained when the explosive was detonated in a vacuum. The curve shows the regular manner in which the percentage of carbon monoxide increases with the weight of acid over this range. It is evident that under these conditions no appreciable "after-ignition" has taken place. When the weight of explosive exceeds 12 grams the percentages of carbon monoxide become irregular and in general less than the values obtained in a vacuum. The break in the curve which occurs at about this point indicates that ignition with the air now takes place to a greater or less extent. When picric acid was detonated in the containers (1·0 inch in diameter), ignition was found to occur even with the smallest weight taken, for example, with 8 grams of explosive. Also a detonation in a container, with internal diameter 1 inch and walls 0·625 inch thick, that is, with the same ratio of diameter to thickness as in series I, gave when loaded with 9·672 grams of picric acid, 0·68 per cent. of carbon monoxide. The low percentage of carbon monoxide shows that ignition has taken place.

The minimum percentage of carbon monoxide is obtained when 20 grams of explosive are detonated in the bomb. Above this weight the percentage rises (curve) until with 47 grams nearly 4 per cent. of this gas is present in the final gaseous mixture. The increase in the percentage of carbon monoxide as the weight of explosive increases may be ascribed to an increased dissociation of carbon dioxide as the excess of oxygen diminishes, or to an irregular admixture of the hot combustible gases with the air of the bomb. The cooling of these gases by radiation of heat to the walls takes place so rapidly that an appreciable amount of the carbon monoxide escapes combustion during the cooling process.

From the figures in Table I, it will be observed that the hot gases from the detonation may burn in the air if the weight of explosive exceeds 12 grams. This is approximately the limiting weight for the conditions ruling in this series of experiments. The heat of detonation of this amount of explosive suffices to raise the whole mass of air enclosed in the bomb to 500° if no energy is expended on the container or lost by radiation. The actual tem-

perature rise, owing to radiation and other losses, will be much lower than this, and even with larger weights of explosive the calculated temperature of the gaseous mixture would be considerably below the ignition temperature. Thus, if the gaseous products from a detonation had been completely mixed with the air of the bomb within the time of pre-flame, that is, before an appreciable amount of combustion occurred, the break in the curve would be expected to occur, not at 12 grams of explosive, but at some much higher value. The actual volume of air with which the gases mix before combustion occurs to any appreciable extent cannot be determined from the above results.

Part II. Explosion of Mixtures of Acetylene and Oxygen.

Mixtures of acetylene and oxygen, contained in thin glass bulbs, were exploded in a small bomb containing air. The glass bulbs were shattered by the explosion and the gaseous products rapidly admixed with the air in the bomb. In order that *combustible* gaseous products with varying compositions and temperatures might be obtained, the proportions and total amounts of the components of the explosive gas mixtures were varied. It was expected that the amount of " after ignition " which occurred would be dependent on these factors. It was found, under the conditions of our experiments, that the gaseous products of the explosion always ignited in the air, although the combustion was never complete. Thus carbon monoxide, acetylene, and methane were present in the final gaseous mixture. For mixtures of acetylene and oxygen in the ratios 1 : 1, 2 : 1, and 3 : 1, about 6—8 per cent. of the acetylene was converted into carbon monoxide, whatever the quantities of the combustible gases and their pressures in the glass bulbs. As would be expected, those mixtures richer in oxygen gave somewhat smaller percentages of carbon monoxide. The maximum percentage of carbon monoxide was obtained with that mixture possessing the highest velocity of explosion.

It is difficult to understand why the amount of " after ignition " should be practically independent of the amounts of acetylene taken. The slow rate at which carbon monoxide and air mixtures burn (Bone and Haward, *Proc. Roy. Soc.*, 1921, [*A*], **100**, 67) is conceivably the cause of the incompleteness of the ignition. One of the intermediate steps in the oxidation of acetylene is the formation of carbon monoxide, and this stage in the oxidation takes place more rapidly than the subsequent conversion of the carbon monoxide into carbon dioxide. In our experiments, the combustion to carbon monoxide is probably complete before the hot gases from the bulb strike the walls of the bomb after the explosion

and the whole of the space is thus filled with a carbon monoxide–air mixture. A definite fraction of this gas, about 6—8 per cent., is chilled by the cold air and the walls of the bomb.

The dilution of the products was not sufficiently rapid to prevent ignition even in those experiments where the heat liberated was insufficient to raise the whole of the gases in the bomb (air and combustible products) to their normal ignition temperature. A true detonation wave is not set up in mixtures of acetylene and oxygen within a distance of 2·5 inches (Dixon, *Phil. Trans.*, 1903, [*A*], **200**, 315), and since this distance is greater than the radius of the largest bulbs, the velocity of propagation of the explosion wave may not have exceeded the velocity of uniform movement of the flame. However, it is probable that the amount of after ignition could be reduced and even avoided altogether, as occurred in the above experiments with picric acid, provided that a detonation wave be set up in the mixture.

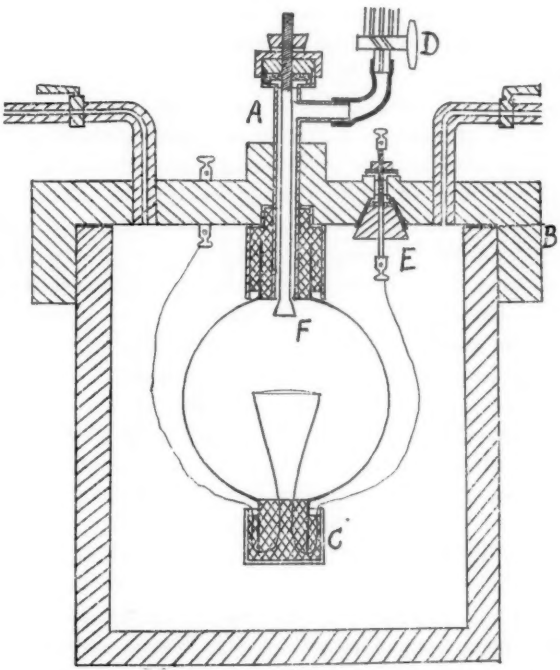
An apparatus has been devised (Fig. 2) which is suitable for the study of the rapid chilling of the products of gaseous explosions. It is hoped that the apparatus will render possible the isolation of some of the intermediate compounds produced during the various stages of the combustion of hydrocarbons. That such compounds are produced by this method was shown in a series of experiments, in which mixtures rich in acetylene were exploded in a thin glass bulb surrounded by an atmosphere of nitrogen. A gaseous product was obtained which exerted a strong reducing action on a solution of ammoniacal silver nitrate. This substance does not appear to be an aldehyde, since it is without effect on Schiff's reagent.

Experimental.

Apparatus.—A diagram of the bomb, with a glass bulb in position, is given in Fig. 2. The bomb consisted of a cylindrical vessel of phosphor-bronze of 1600 c.c. capacity with an internal diameter of 12·7 cm. and an internal height of 12·5 cm. The top of the bomb carried three gas outlets, an insulation plug, *E*, and an earthed terminal. The outlet, *A*, which could be closed by a coned joint at the bottom, was used for the evacuation and filling of the glass bulbs with the mixtures of gases. The glass bulb, terminated at each end by short lengths of glass tubing, was closed at the lower end, *C*, by means of fusible alloy contained in a small brass cup of 1 inch depth and $\frac{3}{4}$ inch diameter. Two enamelled copper wires, used in firing the gaseous mixture, passed through the fusible alloy in this cup into the centre of the bulb. The insulated wires carried a piece of fine iron wire, which could be readily fused by a current from an 8-volt battery. The top end of the bulb was immersed

in another fusible alloy cup attached to the outlet *A* in the top of the bomb. In making the glass-to-metal joints, the fusible metal was heated at 100°, poured into the heated brass cups, and the end of the glass bulb inserted. The fusible alloy was raised by suction to the levels, marked on the glass side tubes, between which the volume of the bulb had been determined and maintained at these points until the metal had solidified. This method of sealing gave vacuum-tight joints, but occasionally some of the bulbs cracked under the strain set up by the solidifying fusible

FIG. 2.



alloy. The weight of a 90 c.c. bulb was about 5 grams and the glass side tubes accounted for the larger proportion of this weight, the bulbs being made as thin as possible.

In carrying out an experiment, a glass bulb of known capacity was cemented in position and the bomb closed by making the joint *B*. The air in the bomb was adjusted to atmospheric pressure and the bulb evacuated through the outlet *A* and the three-way tap, *D*. Mixtures of acetylene and oxygen, saturated with water vapour, were introduced into the bulb at atmospheric pressure, through the other arm of the three-way tap, *D*, which was then

closed and the cone *F* was raised to close the end of the outlet tube. The gases were fired by the fusion of thin iron wire carried by enamelled copper leads passing through the bottom fusible-alloy cup attached to the bulb. After firing, the bomb was allowed to cool to room temperature and the pressure of the gases measured. About 500 c.c. of these gases were removed for analysis and the pressure was again measured. From the difference between the two pressures, the exact volume removed could be calculated. A determination of the ratio of carbon dioxide to carbon monoxide gave a measure of the amount of "after ignition" which had occurred.

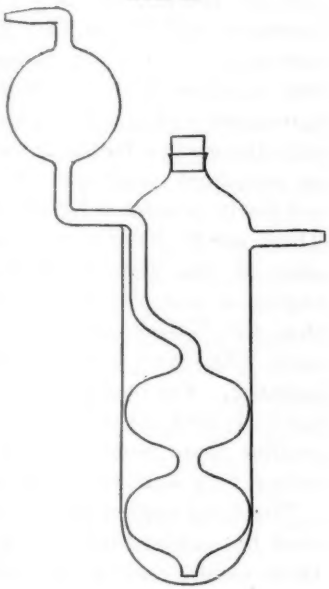
The accuracy of the methods of mixing was checked by analysis of several acetylene–oxygen mixtures after dilution with nitrogen over copper oxide.

Analysis of the Gaseous Products.—The iodine pentoxide method for the analysis of gaseous mixtures containing small quantities of carbon dioxide, carbon monoxide, acetylene, and saturated hydrocarbons offers considerable difficulties. The main source of uncertainty is the removal of the acetylene before passage of the mixture over iodine pentoxide. Levy (*J. Soc. Chem. Ind.*, 1911, **30**, 1437) recommends the use of a solution of bromine in potassium bromide for this purpose. This method was adopted for the majority of the results reported in this paper (Tables III, IV, and V). Experiments carried out in the course of this work have shown, however, that about 30 per cent. of the acetylene in a 1·5 per cent. mixture with air is not retained by this reagent. Possibly volatile bromides or unchanged acetylene pass through the alkali and thence to the iodine pentoxide. Recently Sinnatt and Slater (*Fuel*, 1922, **1**, 241) have drawn the same conclusion, and instead recommend fuming sulphuric acid, which they state is satisfactory. This absorbent was discarded in the present work on account of the sulphur trioxide fume. To avoid the use of this reagent, a method of separation was developed involving the freezing out of the carbon dioxide and the acetylene from the carbon monoxide and saturated hydrocarbons by passing the gases through a spiral immersed in liquid air. Carbon monoxide is not retained by the solid mixture of carbon dioxide and acetylene. The carbon dioxide was usually determined by absorption in baryta solution before freezing out the acetylene.

In the series of experiments described below (Tables III, IV, and V), in which an analysis was made of carbon monoxide, carbon dioxide, and saturated hydrocarbons, it was assumed that the acetylene could be removed completely by bromine in potassium bromide, and the carbon monoxide was estimated by the iodine

pentoxide method. On this account, the percentages of carbon monoxide obtained in this series may be a little too high, by about 0·2 per cent. The results have, however, been checked in some cases by the freezing-out method (see p. 68). The carbon dioxide was removed by passing through two bubblers containing $N/5$-baryta solution, and the carbon monoxide converted into dioxide over iodine pentoxide at 140° according to Levy's method. After passing through a cooling worm containing a little mercury and immersed in ice, the carbon dioxide from the oxidation of the carbon monoxide was absorbed in two more bubblers containing $N/10$-baryta solution. Saturated hydrocarbons were estimated by combustion over copper oxide in silica tubes and the absorption of the carbon dioxide produced in $N/10$-baryta solution. The type of the absorption bubbler employed is shown in Fig. 3, as this type permitted the titration of the excess baryta without risk of introducing carbon dioxide from the air. Burettes could be inserted very quickly into the narrow necks of these bubblers, and during the titration the solution could be stirred by drawing a slow current of carbon dioxide-free air through the apparatus. The air space between the bulbs and the walls of these bubblers should be as small as possible. On account of the difficulty of removing the gas dissolved in the solutions in the bubblers and the large volume of air, which had to be displaced in the analysing apparatus, each complete analysis took about six hours.

FIG. 3.



Results.—The results obtained when the gaseous mixtures were exploded in an atmosphere of air are given in Table III. The nature of the metamorphosis of the explosive mixtures varied to some extent from one experiment to another, depending on conditions governing the fragmentation of the bulb which were not under our control, and it was necessary to carry out a number of experiments under each set of conditions. Typical results are given in each case.

The percentage of acetylene converted into carbon dioxide and carbon monoxide and the ratio $[CO_2]/[CO]$ are given for a number

TABLE III.

Bomb filled with Air.

Gas mixture.	Vol. of bulb in c.c.	Vol. of dry gas at *N.T.P.*	C.c. of CO_2 at *N.T.P.*	C.c. of CO at *N.T.P.*	% of original C_2H_2 appearing as CO_2.	% of original C_2H_2 appearing as CO.	% of original C_2H_2 appearing as Carbon.	$\frac{[CO_2]}{[CO]}$.
$3O_2+C_2H_2$	95·70	90·0	44·0	1·7	97·8	3·8	Nil	25·9
$2O_2+C_2H_2$	94·80	88·2	55·1	2·9	93·7	4·9	Nil	19·0
$O_2+C_2H_2$	90·80	84·9	75·0	7·1	88·3	8·4	Nil	10·6
$O_2+2C_2H_2$	92·70	87·3	102·1	8·2	87·7	7·0	4·9	12·5
$O_2+3C_2H_2$	88·3	83·7	95·5	7·3	76·1	5·8	6·3	13·1

of mixtures of acetylene and oxygen. The ratio decreases from 25·9 for the mixture $3O_2 + C_2H_2$ to 10·6 for $O_2 + C_2H_2$ and then increases slightly to 13·1 for $O_2 + 3C_2H_2$. This ratio is thus a minimum and the percentage of carbon monoxide a maximum for that mixture with the highest velocity of explosion. This is in agreement with the view expressed above, that the rate of admixture with the air is a factor in the phenomena of ignition. Occasionally an abnormal result was obtained, and in these cases the bulb was not finely powdered by the explosion, but broken into large pieces. These results have been omitted from the summary. The appearance of the glass in these cases suggested that the velocity of explosion was abnormally low, and consequently it was expected that the "after ignition" would be greater than usual and the ratio $[CO_2]/[CO]$ higher. This was found to be the case in every instance. For one particular result with the mixture $O_2 + 3C_2H_2$, the ratio $[CO_2]/[CO]$ rose to 86·0 and the carbon deposit was much smaller than usual, the large pieces of glass being covered with only a very light covering of carbon.

The total carbon present in the gases after explosion was estimated by combustion of a sample of gas over copper oxide; from these results and the quantity of acetylene taken, the free carbon given in column 8 has been deduced. These figures are in agreement with the visual examination of the fragments of glass. Except for traces of a dark deposit on the larger glass fragments, there was no evidence of the presence of any carbon in experiments with the first three mixtures, but in the last mixtures the glass was covered by a deposit of carbon, and also the walls of the bomb were frequently covered with a fine carbon dust. Methane or other saturated hydrocarbons were usually present to 0—2 per cent. A visible precipitate of silver acetylide was obtained when the gases from mixtures rich in acetylene were passed through ammoniacal silver nitrate.

The ratio $[CO_2]/[CO]$ was slightly affected by variations in the size of the bulb (Table IV), decreasing from 12·3 to 9·1 as the size

of the bulb changed from 32·0 to 175 c.c. This may be due to an increasing velocity of flame as the volume of gas is augmented. The percentage of acetylene converted into carbon monoxide was practically unaffected by changes in the ratio of the volume of explosive mixture to the volume of air. A series of results obtained for $O_2 + C_2H_2$ mixtures is given in Table IV.

TABLE IV.

Bomb filled with Air.

Gas mixture $C_2H_2 + O_2$.

Size of bulb in c.c.	% of C_2H_2 appearing as CO.	$[CO_2]/[CO]$.	Size of bulb in c.c.	% of C_2H_2 appearing as CO.	$[CO_2]/[CO]$.
32·0	7·6	12·3	115·0	7·3	11·0
61·0	7·8	12·0	150·0	7·7	9·4
90·8	8·4	10·6	175·0	9·0	9·1

In one experiment, the pressure of the gaseous mixture was increased to 130 cm. of mercury, and here the percentage of acetylene converted into carbon monoxide was 7·3, compared with 8·4 for atmospheric pressure.

A series of experiments (Table V), in which the air in the bomb was replaced with nitrogen gave a gaseous product, which readily reduced ammoniacal silver nitrate solution. From the mixtures $3C_2H_2 + O_2$ and $2C_2H_2 + O_2$ a large, black precipitate was obtained, but the amounts of this reducing substance were variable from one experiment to another. The reducing substance did not appear to be an aldehyde, but time was not available for its complete investigation. From mixtures richer in oxygen, blue colloidal silver sols were obtained.

The results obtained with $O_2 + C_2H_2$ mixtures agree with those of Bone and Drugman (T., 1906, **89**, 660).

TABLE V.

Bomb filled with Nitrogen.

Gas mixture.	Vol. of bulb in c.c.	Vol. of dry gas at *N.T.P.*	C.c. of CO_2 at *N.T.P.*	C.c. of CO at *N.T.P.*	% of original C_2H_2 appearing as CO_2.	% of original C_2H_2 appearing as CO.	$[CO_2]/[CO]$.
$3O_2+C_2H_2$	87·7	82·8	37·1	3·7	89·6	8·9	10·1
$2O_2+C_2H_2$	88·0	82·2	30·6	23·1	55·8	42·2	1·3
$O_2+C_2H_2$	92·3	86·6	1·1	84·0	1·3	97·0	0·01
$O_2+2C_2H_2$	87·2	81·5	Nil	53·8	Nil	49·5	
$O_2+3C_2H_2$	88·7	81·1	Nil	43·4	Nil	35·7 *	

* This percentage may include a small amount of the reducing substance, as this was not removed during the analysis.

A further series of experiments has been carried out by Mr. R. G. Fitter, in which the acetylene was condensed out of the gaseous

mixture after removal of the carbon dioxide by passing the gaseous products through a spiral immersed in liquid air, and the carbon monoxide and methane were converted into carbon dioxide over copper oxide. The total percentage of carbon monoxide and saturated hydrocarbons recorded by this method is somewhat higher than that obtained for carbon monoxide by the iodine pentoxide method. Thus for $C_2H_2 + O_2$, 9·3 per cent. against 8·4 per cent., for $2C_2H_2 + O_2$, 9·07 per cent. against 7·0 per cent., and for $3C_2H_2 + O_2$, 8·8 per cent. against 5·8 per cent., but allowing for the methane included in this percentage the confirmation of the results of the first series may be regarded as satisfactory.

Remarks on Part II.

The explosion of acetylene and oxygen mixtures in thin glass bulbs gives rise to gaseous products which inflame in the air of a closed vessel. The " after ignition " is only partial, about 6—8 per cent. of the total hydrocarbon being converted into carbon monoxide. The conversion into carbon monoxide is slightly affected by changes in the ratio of the volume of explosive mixture to the volume of air. The degree of chilling is at a maximum and the ratio $[CO_2]/[CO]$ at a minimum for the mixture possessing the maximum velocity of combustion. Free carbon is produced from mixtures containing less than equimolecular proportions of oxygen, and small percentages of acetylene and saturated hydrocarbons are found in the products of the explosion.

The conditions under which these explosions are carried out should be favourable to the appearance of carbon if this is one of the initial products in the combustion of acetylene in oxygen. Carbon was only observed in those experiments where there was insufficient oxygen to convert all the carbon into carbon monoxide. The absence of carbon from the products of the explosion of the first three mixtures confirms Bone's view of the mechanism of the combustion of hydrocarbons. According to this view, oxidation of the hydrocarbon takes place through aldehydes and acids to carbon dioxide, without the liberation of carbon at any of the stages of combustion.

Summary.

Experiments have been described in which high explosives in steel containers, and acetylene and oxygen mixtures in glass bulbs, have been exploded in a limited volume of air. The products have been analysed to determine the degree of ignition which occurs. It is shown, in the case of high explosives, that the phenomenon of " after ignition " is to some extent determined by the volume of air into which the gases are projected, ignition occurring

when the ratio of weight of explosive to volume of air exceeds a definite value. The interpretation of the results is rendered difficult by the unknown amount of cooling brought about by the disruption of the container. On the other hand, the gaseous products from the acetylene–oxygen mixtures, on account of their much slower rates of explosion as compared with the velocity of detonation of high explosives, always underwent partial ignition on admixture with air, and the degree of ignition is dependent to some degree on the ratio of volume of air to volume of explosive, and slightly affected by changes in the composition of the gaseous mixture. The ignition is the more complete the slower the velocity of explosion of the gases, and this confirms the view that the ignition temperature of hot gases projected into cold air is dependent on the rapidity of admixture.

We wish to express our best thanks to the Director of Artillery for permission to publish that part of this work carried out at the Research Department, Royal Arsenal, Woolwich, and to the Department of Scientific and Industrial Research for a grant to one of us.

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THE RESEARCH DEPARTMENT,
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IX.—*The Dissociation Constant of Boric Acid.*

By EDMUND BRYDGES RUDHALL PRIDEAUX and ALFRED THOMAS WARD.

ON account of their utility as buffer mixtures, various borate solutions have been standardised with the hydrogen electrode, and from these results the apparent dissociation constants of boric acid in these solutions may be calculated. Such constants depend on the agreed status of the hydrogen electrode as representing the best measure yet available of the activity of the hydrogen-ion. If the activities, or effective concentrations, of the ion and the undissociated acid are put equal to the neutralised and the unneutralised part of the acid respectively, complete dissociation of the salts is assumed. The constants are then apparent constants, useful in the calculation of the p_H of mixtures not too far removed in concentration from the standards. The apparent constant is calculated by the usual equation, which is conveniently stated in

the form $k = Rh/(1 - R)$, in which R is the ratio of equivalents of alkali to mols. of acid.

It is usually found that k varies with (1) degree of neutralisation, (2) total concentration, and (3) presence of neutral salts.

(1) The following results refer to borax, NaH_2BO_3,H_3BO_3, in which R is 0·5 and $h = k$, $p_H = p_k$.

	Schmidt and Finger.	Sorensen.	Palitzsch.	Clark and Lubs.
C	0·25	0·10	0·05	0·05 (0·2 KCl)
p_H	9·3	9·24	9·24	9·14
$k \times 10^{10}$	5·0	5·6	5·6	7·2

The authors, at $C = 0·02$, find $p_H = 9·02$ and $k \times 10^{10} = 9·55$.

A decrease in total concentration thus brings about an increase in k. This change is in the opposite direction to that which has been noted in the case of phosphoric acid (second constant).

The result for boric acid may perhaps be attributed to the breaking up of the anionic complexes H_2BO_3',nH_3BO_3, which are formed in partly neutralised borate solutions, especially at higher concentrations (Auerbach, *Z. anorg. Chem.*, 1904, **37**, 352; Prideaux, *Trans. Faraday Soc.*, 1915, **15**, 76).

In the most dilute solutions the constant is not far from the conductivity constant, $1·7 \times 10^{-9}$.

(2) The change in k with degree of neutralisation R may be obtained from the results of Palitzsch and of Clark and Lubs.

We have added some determinations in more dilute solutions. Palitzsch's solutions were made from 0·2M-boric acid mixed with 0·02M-borax. The total concentrations were therefore not constant.

C.c. of borax/c.c. of boric acid	0·3/9·7	9·6/9·4	8·0/2·0	9·0/1·0
C	0·196	0·195	0·080	0·065
R	0·00383	0·007	0·25	0·345
$k \times 10^{10}$	6·5	5·75	3·6	4·1

Clark and Lubs's solutions were made by adding 0·2N-sodium hydroxide to 50 c.c. of 0·2M-boric acid and diluting to 200 c.c. They were therefore 0·05 molar with respect to borate.

C.c. of sodium hydroxide/50 c.c. of boric acid	2·61	12·00	21·30	26·70	43·90
p_H	7·8	8·6	9·0	9·2	10·0
$k \times 10^{10}$	8·4	7·9	7·4	7·4	7·1

Our solutions were 0·02 molar with respect to borate and 0·06 molar with respect to sodium chloride. The temperature was about 18°.

R	0·25	0·50	0·75
p_H	8·54	9·02	9·56
p_k	9·02	9·02	9·08
$k \times 10^{10}$	9·6	9·6	8·25

In each series an increase in R is associated with a decrease in k. Also, by comparison (at corresponding concentrations) of

series 1 with 2 and 3 respectively, it is seen that the addition of neutral salt increases k.

The Constant of Boric Acid Calculated from the Ionic Activities.

The activity of the hydrion is taken as that given by the hydrogen electrode, and the activities of the H_2BO_3'-ion as that of ClO_3' in solutions of the same ionic strength, as given in the tables of Lewis and Randall's "Thermodynamics." * By means of the activity coefficients, a, we get an expression for the ion activity constant $k' = ha[A]/a[HA]$.

The activity of the undissociated molecule, in this case H_3BO_3, may perhaps be taken as 1 in dilute solutions by analogy with glycerol and other non-electrolytes. In more concentrated solutions it would be greater than unity. The equation given in Lewis and Randall's book (p. 288), when applied to the freezing-point depression of a 0·066 molar solution of boric acid, 0·129° (Juttner-Arrhenius), gives an activity coefficient of 1·094. On this account, and because the ionic strengths in the buffer solutions quoted above are too high for the application of Lewis and Randall's tables, the calculations must be restricted to the solutions measured by us.

At $R = 0{\cdot}5$, $C_{\text{borate}} = 0{\cdot}02$ and $C_{\text{NaCl}} = 0{\cdot}06$. $[H_2BO_3'] = 0{\cdot}01$.

The total ionic strength is equal to half the sum of $Na^{\cdot} = 0{\cdot}07$, $Cl' = 0{\cdot}06$, $H_2BO_3' = 0{\cdot}01$, that is, to 0·07.

The activity of H_2BO_3' is taken as that of ClO_3' at this ionic strength, that is, 0·65.

$$\text{Then } k = \frac{h[H_2BO_3']a_1}{[H_3BO_3]} = \frac{9{\cdot}6\ 10^{-10} \times 0{\cdot}0065}{0{\cdot}01} = 6{\cdot}2 \times 10^{-10}.$$

$R =$	0·25	0·50	0·75
$k \times 10^{10} =$	6·3	6·2	5·3

The ion activity constant which allows for the effect of all ions present is thus smaller than the apparent constant calculated for the dilute borate. It happens to agree with the constant usually attributed to boric acid. The ion activity constant still shows a fall at higher values of R. We consider that this is to be accounted for in the same manner as the fall in the apparent constant. The correction for ionic strengths does not take account of complex ions.

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* In these tables the concentrations are expressed in molalities or mols. in 1,000 grams of water. We have expressed them in mols. per litre, the numerics being almost identical in such dilute solutions.

X.—*The Reaction between Copper and Nitrogen Peroxide.*

By James Ritchie Park and James Riddick Partington.

Sabatier and Senderens (*Compt. rend.*, 1892, **115**, 236; 1893, **116**, 756) observed that reduced copper absorbs gaseous nitrogen dioxide with evolution of heat, the product being a maroon-coloured substance, the composition of which they represented by the formula Cu_2NO_2 (Found: Cu = 73·0; NO_2 = 26·8, 26·5, 26·4. Calc., Cu = 73·4; NO_2 = 26·6 per cent.).

The " Cuivre Nitré " (nitro-copper) reacted violently with water, nitric oxide being evolved. A green liquid, containing cupric nitrate and a little nitrite, was left, together with a residue of nearly 60 per cent. of the original copper.

On heating in pure dry nitrogen at 70°, or in a closed tube, nitrogen dioxide was evolved, and copper remained, mixed with a certain amount of oxide. The oxygen in this residue was found to be 6·16 per cent. Partial readsorption on cooling was observed. Complete absence of all traces of nitric acid or moisture is essential, these reacting to form green nitrate.

Sabatier and Senderens remark that nitric oxide is mixed with the nitrogen peroxide evolved on heating, whilst even nitrogen is obtained on rapid heating. In their second paper, some chemical properties of the nitro-copper are described. Hydrogen was without action in the cold, but at 180° abundant evolution of ammonium nitrite and free ammonia took place. Carbon monoxide on slow heating gave reduced copper, nitrogen peroxide being evolved. Sulphur dioxide had no specific action, but reacted with the nitrogen peroxide evolved to give crystals (evidently chamber crystals) in the cold part of the tube. Ammonia reacted immediately in the cold, white fumes of ammonium nitrite and nitrate, together with water vapour, being evolved. The heat of the reaction caused incandescence. A residue of copper oxide and cuprammonium oxide was left. Hydrogen sulphide reacted in the cold, with evolution of heat, to form water and sulphur, leaving copper sulphide.

It is evident that the reactions of the substance are those of nitrogen peroxide, and all the results could be explained on the assumption that the nitrogen peroxide is merely adsorbed and reacts as such.

There is no further reference to this reaction until 1921, when it was investigated by Tartar and Semon (*J. Amer. Chem. Soc.*, 1921, **43**, 494).* They prepared reduced copper by reducing ignited

* Work on the substance by one of the authors (J. R. P.) and D. B. Huntingford was well advanced when Tartar and Semon's paper appeared. Since quite different results had been obtained, the investigation was continued.

cupric oxide with hydrogen or carbon monoxide, or by reducing the compound $4Cu_2O,H_2O$ with either gas. The reduced copper having cooled to 25—27° in an atmosphere of nitrogen, nitrogen peroxide was passed in.

The quantity of nitrogen peroxide absorbed by the copper was ascertained by the gain in weight, and was very variable, absorption ceasing in many cases only after two or three days. The total percentage of nitrogen and oxygen in the product varied from 7 to 27. Copper reduced by carbon monoxide did not react at once, and required several days' treatment for the reaction to reach completion, whilst copper reduced by hydrogen reacted immediately and fairly rapidly. The copper first darkened to chestnut brown and finally turned green in places. Only 5 per cent. absorption was obtained when copper was treated with a saturated solution of nitrogen peroxide in dry benzene.

Since there was apparently no relation between the weight of copper and the gain in weight, the ratio between the numbers of atoms of nitrogen and oxygen in the final product was found. The mean value of ratio O/N was 3 : 1 (2·89 to 3·19) if the product was analysed immediately. If the product was allowed to stand in a desiccator over calcium chloride previous to analysis, a ratio O/N greater than 3 : 1 was obtained, due to evolution of oxides of nitrogen, and a residue containing copper oxide was left. Sabatier and Senderens's statement that 60 per cent. of the copper remained in the free state on treatment of the product with water was confirmed. Microscopic examination showed metallic particles of copper embedded in a matrix of "brownish material."

Guntz and Martin (*Bull. Soc. chim.*, 1909, [iv], **5**, 1104; 1910, [iv], **7**, 313) described anhydrous cupric nitrate as a very deliquescent *white* powder with a blue tinge, and Tartar and Semon suggest that the product is anhydrous *cuprous* nitrate formed on the surface of unchanged copper. This would agree with the O/N ratio, but is supported by no other evidence.

An interesting experiment, which appears to have escaped notice, is due to Divers and Shimidzu (T., 1885, **47**, 633). They poured liquid nitrogen tetroxide on reduced copper, and observed an immediate action with brisk effervescence; nitric oxide was evolved, and the copper turned grey with a blue or green tinge. The excess of nitrogen peroxide turned deep green, and as this vanished on partial evaporation, it could not be due to dissolved copper salt. The product of the reaction was believed to be cuprous nitrate mixed with a little cupric nitrate, although no analysis is given. In one experiment, the copper had taken up one-fifth of its weight

of nitrogen peroxide. This experiment is significant in showing that reduction of nitrogen peroxide takes place.

Experimental.

Nitrogen Peroxide.—One hundred c.c. of fuming nitric acid contained in a retort cooled in a freezing mixture were slowly saturated with sulphur dioxide until the whole set to a mass of nitrososulphuric acid. Dry powdered potassium nitrate (240 grams) was added, and the mixture distilled, the vapours evolved being condensed in a worm condenser cooled in a freezing mixture, and the product collected in a receiver cooled in a similar manner. All joints were sealed with asbestos and paraffin wax. The condensed liquid, deep green in the first portions, but finally straw-yellow, was collected in bulbs and sealed off. The crude tetroxide was then fractionated with excess of phosphoric oxide in a similar apparatus, including a still-head of the pear type, having 8 bulbs. The main distillate, boiling at 21·5—22·5°, of a light brown colour, was collected in bulbs and sealed off.

Reduced Copper.—This was prepared by reducing at a low temperature a basic cupric nitrate precipitated by dilute ammonia from cupric nitrate. The gelatinous basic salt was washed repeatedly with warm water until the washings gave no further reaction for copper, nitrate, or ammonia, and dried at 80—90°. The resulting substance was an extremely finely-divided, light greenish-blue powder, having the composition $Cu(NO_3)_2,3Cu(OH)_2$ (Found : Cu = 52·69 per cent.).*

Apparatus.—A glass cylindrical vessel, *A*, Fig. 1, 5 × 1 in., was fitted at each end with a Y-piece, each arm of which carried a tap and ground joint. The four arms of the Y-pieces, *P*, *Q*, *R*, and *S*, made connexion by means of ground joints with the remaining apparatus.

Hydrogen was generated by the electrolysis of a saturated solution of barium hydroxide at 100°, with sheet nickel electrodes, in a large Jena † flask, *B*. The cathode was surrounded by a cylindrical glass diaphragm. The hydrogen was passed through dilute sulphuric acid (*C*), quicklime (*D*), heated platinised asbestos (*E*), calcium chloride (*F*), and phosphoric oxide (*G*), and so to the arm *P* of the Y-tube.

Carbon dioxide generated by heating sodium bicarbonate was dried by calcium chloride and the tubes *F* and *G*.

Nitrogen was roughly dried by sulphuric acid (*H*), passed through

* Compare Roscoe and Schorlemmer, Vol. 2, p. 453 (1923).

† Jena glass alone was capable of resisting the attack of the baryta. Platinum electrodes were rapidly disintegrated.

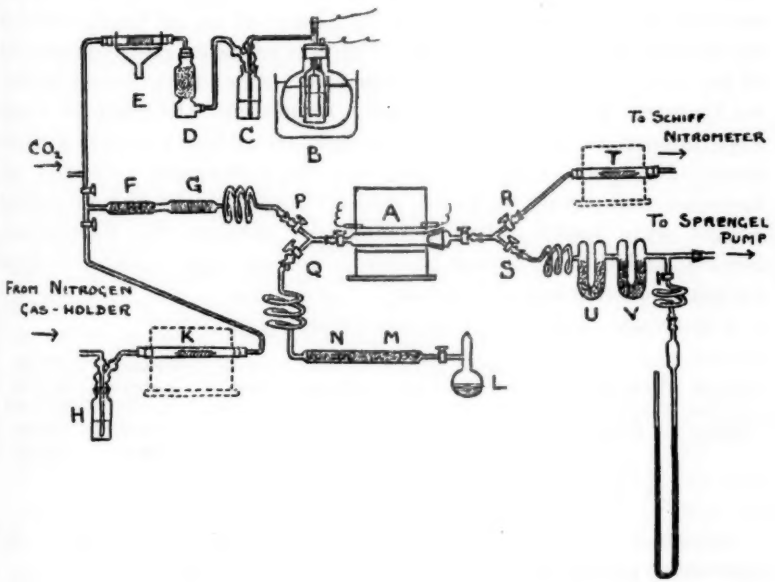
a hard-glass tube, K, containing spirals of copper gauze heated to redness, and was then dried by passing through F and G.

Liquid nitrogen peroxide was sealed in a flask, L. The gas was passed over dry granular copper oxide, M, to remove traces of nitric acid, and dried by phosphoric oxide, N.

R connected with a hard-glass tube, T, containing copper spirals, strongly heated. The exit tube led to a Schiff nitrometer.

S made connexion through U-tubes containing phosphoric oxide, U, and pumice soaked in concentrated sulphuric acid, V, with a Sprengel pump and manometer.

FIG. 1.



All joints were of ground glass, lubricated with the smallest quantity of vaseline, except the tube T, of which the two ends were fitted with rubber stoppers.

Rate of Absorption of Nitrogen Peroxide by Copper.

The evacuated vessel, A, and the empty porcelain boat were weighed, the boat then filled with basic cupric nitrate and replaced in the vessel A, which was again evacuated and weighed.

The apparatus was connected as shown, the taps in P and S being opened. When the hydrogen had displaced all air from the apparatus, the electric furnace surrounding A was brought into action. On the temperature reaching about 180° (measured by a mercury

thermometer), the substance in the boat blackened, water and some nitrogen peroxide being evolved, and the cupric oxide thus obtained began to reduce at 300°. The temperature was then lowered to about 270°, and the main reduction completed. Reduction was carried out at as low a temperature as possible to prevent the finely divided copper sintering together. The boat and contents were cooled in a current of hydrogen, and the tube was again weighed vacuous. The copper was of a fine spongy texture.

A slow stream of nitrogen peroxide was then passed through *A*, the excess being absorbed in *V*. The copper slowly darkened to a deep brown colour, the reaction evolving a perceptible amount of heat.* After fifteen minutes, when all the copper had darkened, the tube was rapidly evacuated by means of an oil pump behind the manometer, and reweighed. This was repeated after an interval of an hour, and later at longer intervals. After twenty-four hours, no increase in weight was usually noticeable, although in some experiments the slow increase in weight continued for two or three days. No green specks formed on the substance provided all moisture was rigidly excluded, and no bright specks of unattacked copper were visible. The green specks obtained by Tartar and Semon probably consisted of cupric nitrate and nitrite, formed by unexcluded traces of moisture.

The results of the first experiments are given below.

Gram of Cu.	Time of reaction.	Gram of copper compd.	% N and O absorbed.	Gram of Cu.	Time of reaction.	Gram of copper compd.	% N and O absorbed.
0·3005	½ hr.	0·3679	18·32	0·1552	18 hrs.	0·2075	25·20
	1 „	0·4575	34·32		2 days	0·2663	41·72
	3 hrs.	0·5420	44·55		3 „	0·2715	42·84
	24 „	0·5451	44·87				

(The highest percentage of nitrogen and oxygen contained in the specimens prepared by previous workers was 27·2.)

Absorption, rapid at first, slowed down until the maximum, practically 45 per cent., was reached. The composition of the nitro-copper was variable, but the formula Cu_2NO_2 proposed by Sabatier and Senderens is clearly untenable, since it would correspond with a maximum absorption of only 26·6 per cent.

For the estimation of nitrogen and oxygen in the substance the method used by Sabatier and Senderens was employed, the gases evolved on heating being passed over strongly heated copper, and the nitrogen collected in a Schiff nitrometer.

The sodium bicarbonate tube was heated, and the carbon dioxide

* When the reaction was later carried out with several grams of copper, the heat evolved was very considerable, the temperature of the vessel rising to 50—60°.

passed through the vessel *A*, and the tube *T*, containing bright copper gauze spirals, heated to *bright redness*.* The furnace heating *A* was then switched on, and the temperature raised to 90° to 100°. Brown fumes were evolved, and passed into *T*, the nitrogen passing to the nitrometer. When the evolution of gas ceased, the temperature of *A* was raised to 150° to ensure complete decomposition of the substance. *A* was allowed to cool in a current of carbon dioxide, exhausted and weighed. (In subsequent experiments, it was found preferable to weigh *A* filled with nitrogen.)

The total weight of nitrogen and oxygen being known, and the weight of nitrogen obtained from the volume collected, the oxygen was determined by difference.

Atomic Ratios O/N.—

Experiment	1	2	3	4	5
In the solid	2·73	3·03	2·97	3·26	2·98
In the gas evolved ...	2·21	2·28	2·08	2·23	2·50

The atomic ratio O/N in the solid nitro-copper is also variable, but has a mean value of about 3, agreeing with that found by Tartar and Semon.

The gas evolved on heating, according to the above results, would have a composition $NO_{2\cdot25}$, the nitrogen being rather lower than that required for NO_2. This gas evolved on heating was later shown to be completely absorbable by concentrated sulphuric acid, and no free oxygen was obtained. The difference in the present experiments may have been due to the removal of a certain amount of nitrogen peroxide from the substance during the passing of carbon dioxide before starting the estimation.

The oxygen in the residue had a mean value of 11·1 per cent. The oxygen in cuprous oxide is 11·2 per cent. The residue was therefore further treated to determine whether it consisted of cuprous oxide, or of a mixture of copper and cupric oxide, as previous experiments had stated. It dissolved almost entirely in concentrated hydrochloric acid, only a slight residue of free copper (which had remained unattacked) remaining, giving an almost colourless solution, which turned green on standing, and on addition of water precipitated white cuprous chloride in large quantity. The residue is cuprous oxide.

With the object of determining the composition of the gas evolved on heating, about 1·5 grams of copper were converted into nitro-copper, *A* was then evacuated, and the electric furnace regulated to about 100°, the Sprengel pump was kept steadily working, and all

* Except at high temperatures, appreciable amounts of nitric oxide collect in the nitrometer.

gases were drawn through U and V. The evolved gas was practically completely absorbed by the sulphuric acid, only 7 c.c. of nitrogen being collected (unabsorbed by alkaline pyrogallol and by ferrous sulphate solution). Apparently this was due to a slight leakage of nitrogen from the other side of the tap to the left of A, which had been warmed by the heating of the tube.

If the substance were cuprous nitrate, since the residue is found to be cuprous oxide, the decomposition would be

$$2Cu_2(NO_3)_2 = 2Cu_2O + 4NO_2 + O_2.$$

Two grams of cuprous nitrite (1·8524 grams of substance were used) would yield nearly 90 c.c. of free oxygen. The composition $Cu_2(NO_3)_2$ is therefore untenable.

The experiments described show that the substance yields cuprous oxide and nitrogen peroxide on heating, and a factor in the reaction must of necessity be reduction of the nitrogen peroxide, probably to nitric oxide. The mixture of vapours produced by the action of nitrogen peroxide on copper was next condensed by cooling, and the liquid analysed. The vapours passing out at R were condensed in a 25 c.c. bulb, α (not shown), the two delivery tubes of which were drawn out to fine capillaries. Following this was a U-tube containing pumice and sulphuric acid, to prevent nitrogen peroxide reaching the Schiff nitrometer. At the other end of the apparatus was the carbon dioxide generator. Reduced copper having been prepared in the usual manner and weighed, a current of carbon dioxide was passed through the apparatus. The bulb α was removed and weighed when filled with the gas. The bulb was replaced and was cooled well below $-25°$. By opening Q and slightly warming L, a slow stream of nitrogen peroxide was passed over the copper, the vapour passing on being condensed in α. The copper slowly darkened, and a deep green liquid collected in α, indicating the presence of nitrogen trioxide. No nitric oxide collected in the nitrometer.

After about an hour all taps were closed, and the contents of α sealed up. The bulb, with the two joints removed by sealing, was weighed. Nitrogen peroxide was expelled from A by a stream of nitrogen, and A weighed. Finally the nitro-copper was heated at 150° in nitrogen until all nitrogen peroxide had been driven off, and the bulb and residual cuprous oxide were cooled and weighed as before.

Since the reaction would not be complete in an hour, it was necessary to estimate the amount of copper which had not reacted. The contents of the boat were treated with concentrated hydrochloric acid, the residual copper being washed and ignited to cupric oxide. From these data the weight of cuprous oxide formed could

be calculated. The weight of copper taken was 0·4960 gram, the weight of nitro-copper obtained was 0·7646 gram, the residue on heating weighed 0·5401 gram, and this was found to contain 0·1489 gram of free copper.

The bulb α was now placed in a bottle containing 500 c.c. of 10 per cent. caustic potash solution, the stopper tied down, and the bulb broken by shaking. When the vapours had completely dissolved, the solution was rinsed into a litre flask, and made up to the mark with water.

The total nitrogen content was determined by reduction to ammonia, and the nitrite by titration with permanganate.

The weight of liquid in the bulb α was 4·0242 grams. This was found to contain 3·8114 grams of nitrogen tetroxide and 0·2022 gram of nitrogen trioxide, corresponding with 0·0798 gram of nitric oxide (Total $N_2O_4 + N_2O_3 = 4·0136$ grams).

Now if the primary reaction is $2Cu + NO_2 = NO + Cu_2O$, the weight of cuprous oxide in the residue should correspond with this weight of nitric oxide. The weight of cuprous oxide in the residue was 0·3912 gram, corresponding with $0·3912 \times 30/142 = 0·0826$ gram of nitric oxide, in fairly good agreement, the error being less than 3·5 per cent. This difference is readily accounted for, since nitrogen trioxide is extremely volatile, and a trace would very likely be carried over into the sulphuric acid tube.

It may therefore be safely assumed that the first reaction between copper and nitrogen peroxide results in the formation of cuprous oxide and nitric oxide. The cuprous oxide may or may not undergo further reaction.

The nitro-copper possesses a considerable vapour tension of nitrogen peroxide. This is in itself quite consonant with either of the two theories of the composition of the substance; it may be due either to slow decomposition of an unstable compound or to dissociation of an adsorption complex. For any definite temperature, however, the pressure of a molecular compound has a constant value, whilst that of an adsorption complex is variable, according to the amount of nitrogen peroxide left in it.

The transpiration method was used for the determination of the pressure of the nitro-copper, a known volume of pure dry nitrogen being passed over the substance at such a rate that equilibrium was ensured, and the nitrogen peroxide carried over was absorbed in concentrated sulphuric acid.

The values for the vapour pressure at 23° obtained in these experiments were extremely variable (0·19 to 2·51 mm.). One specimen of nitro-copper yielded much lower values than two others, but the vapour pressure of each specimen decreased, in most

cases, as nitrogen peroxide was removed by transpiration. The results indicated that the substance is probably an adsorption complex, its pressure having different values according to the proportion of nitrogen peroxide adsorbed.

Microscopical Examination.

Under the microscope the extremely fine spongy texture of the reduced copper did not appear to alter after treatment with nitrogen peroxide, although the colour changed from reddish-yellow to deep brown. No particles of unattacked copper, as described by Tartar and Semon, were discernible.

Extraction of Nitrogen Peroxide with Solvents.

Carbon tetrachloride and chloroform were dried by heating under reflux with calcium chloride, decanted, fractionally distilled, and were further dried by standing over phosphoric oxide. Two specimens of nitro-copper, of 3 to 4 grams each, were treated with about 250 c.c. of carbon tetrachloride and chloroform, respectively, in stoppered bottles. Chloroform appeared to react with the substance, the mass slowly turning green and a flocculent precipitate being formed. Carbon tetrachloride, however, gave satisfactory results. The bottle was shaken at intervals and when the solvent was coloured distinctly yellow with nitrogen peroxide, it was poured off and fresh added. This process was repeated for four weeks at room temperature, great care being taken to exclude moisture. The solvent ceased to be coloured, even on standing over the substance for several days. The nitro-copper was then removed, and dried at 30—40° in a current of air. A weighed amount of the dried substance was distilled with potash and Devarda's alloy. At room temperature it was found that more than half of the nitrogen peroxide was removed.

The extraction was carried out at higher temperatures. Four to five grams of the substance, contained in a porous " thimble " previously dried at 120°, were treated with carbon tetrachloride in a Soxhlet apparatus between 65° and 70°, the nitrogen peroxide being removed from each portion of solvent as it siphoned over by means of excess of solid caustic potash in the flask below. All air entering the apparatus at the top of the condenser was dried.

After eight hours, the solvent ceased to be coloured and the residue was removed and dried at 30—40°. It possessed no smell, did not react with water, and evolved no brown fumes of nitrogen peroxide on heating. Its solution in concentrated hydrochloric acid gave all the reactions of cuprous chloride. On distilling with

caustic potash and Devarda's alloy, only a trace of ammonia was recovered, this being probably due to a small amount of cupric nitrate and nitrite, formed by the action of a little moisture on the original substance.

Thus at 65—70°, *all* the nitrogen peroxide contained in the so-called nitro-copper is removable by solvents, leaving a residue of cuprous oxide. This also indicates that the nitrogen peroxide is adsorbed, and not chemically combined.

Conclusions.

The reaction between nitrogen peroxide and reduced copper would appear to proceed as follows. On passing the gas over copper, the latter is oxidised to cuprous oxide with the evolution of heat, the nitrogen peroxide being reduced to nitric oxide :

$$2Cu + NO_2 = Cu_2O + NO.$$

The cuprous oxide then adsorbs nitrogen peroxide up to a saturation point, represented by about 33 per cent. of nitrogen peroxide.

On heating the substance, free nitrogen peroxide is driven off and cuprous oxide remains: readsorption takes place in part on cooling.

The percentage of nitrogen peroxide taken up by copper is variable. The mean value of the atomic ratio O/N is practically 3, as stated by Tartar and Semon, but this varies considerably, and moreover is quite consistent with the formation of cuprous oxide and subsequent adsorption of nitrogen peroxide.

The formulæ Cu_2NO_2 and $Cu_2(NO_3)_2$ suggested by previous workers do not agree with the mode of formation or properties of the substance, whereas these are explained by the reactions now proposed. No oxygen or nitrogen is evolved on decomposition of the nitro-copper by heat.

The reaction with water, in which nitric oxide is evolved and a solution of cupric nitrate, with a little nitrite, left, is not conceivably that of a nitrate, whereas it is quite in agreement with the theory propounded above. The adsorption complex yNO_2,xCu_2O might be expected to react as follows :—

(1) $2NO_2 + H_2O \rightleftharpoons HNO_3 + HNO_2$.
(2) $3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O$.
(3) $3Cu_2O + 14HNO_3 = 6Cu(NO_3)_2 + 2NO + 7H_2O$.

A certain amount of cupric nitrite will be formed by the action of the undecomposed nitrous acid.

The residue of copper found by previous workers had evidently

escaped reaction, since the product contained only 27 per cent. of nitrogen and oxygen as a maximum.

The whole of the nitrogen peroxide is removed by a solvent at 65—70°.

The results as a whole point, in our estimation fairly conclusively, to the conclusion that nitro-copper is merely an adsorption complex of nitrogen peroxide in cuprous oxide.

We wish to thank the Chemical Society for a grant which defrayed most of the expense in connexion with the research. We also wish to thank Mr. D. B. Huntingford for placing at our disposal the apparatus and some preliminary results which he had obtained in 1921.

THE CHEMICAL DEPARTMENT,
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UNIVERSITY OF LONDON. [*Received, October 26th*, 1923.]

XI.—*The Influence of Catalysts on the Production of Potassium Perchlorate by the Action of Heat on Potassium Chlorate.*

By WALTER FARMER and JAMES BRIERLEY FIRTH.

THE object of the present investigation was to examine the influence of certain substances on the yield of potassium perchlorate obtained by the decomposition of potassium chlorate by heat, the conditions of the experiment being directed as far as possible to give the maximum yield of perchlorate.

The existing information shows a lack of agreement between different workers as to the effect of heat on potassium chlorate and the influence of catalysts. Thus Fowler and Grant (T., 1890, **57**, 272) stated that potassium chlorate was oxidised to perchlorate by silver oxide, lead dioxide, and mercuric oxide, whereas Mathers and Aldred (*Trans. Electrochem.*, 1922, **40**, 57) found that the yield of perchlorate was not increased but rather diminished by these substances. They found that 55 per cent. of the chlorate could be converted into perchlorate by heating at 480—550° for a period varying, with the temperature and quantity of chlorate, from thirty minutes to four hours, whilst Blau and Weingand (*Z. Elektrochem.*, 1921, **27**, 1), using a quartz flask, obtained a conversion of 61 per cent.

The experiments herein described show that at temperatures from 280—350° silver oxide undergoes decomposition, but no perchlorate

is formed. At 380°, the decomposition of the oxide is complete, and oxygen is obtained freely from the decomposing chlorate, but only a very small amount of perchlorate is formed in each series. The experiments support the view of Mathers and Aldred (*loc. cit.*) that the yield of perchlorate is not increased by the presence of oxidising agents; on the other hand, many substances are capable of reducing it.

The decomposition of potassium chlorate may be simply represented by the following equations:

(i) $2KClO_3 = 2KCl + 3O_2$. (ii) $2KClO_3 = KClO_4 + KCl + O_2$.
(iii) $4KClO_3 = 3KClO_4 + KCl$.

In (i) no perchlorate is produced, in (ii) the maximum possible conversion to perchlorate is 50 per cent., and in (iii) 75 per cent. The yield of perchlorate would therefore be determined by the particular mode of decomposition.

Normally, at temperatures between 480° and 550°, it would appear that decomposition takes place mainly according to equation (ii), but the introduction of cerium and thorium oxides facilitates reaction (i), whereby the product is almost entirely potassium chloride and oxygen. Zirconium oxide and glass also considerably reduce the yield of perchlorate by facilitating decomposition into chloride and oxygen. Aluminium silicate and potassium dichromate not only considerably reduce the yield of perchlorate, but also appreciably reduce the proportion of chlorate decomposed. The addition of potassium dichromate, according to D.R.-P. 136678, increases the yield of perchlorate. The results obtained in quartz tubes are uniformly higher than those in either glass or porcelain, and by the addition of powdered quartz to the chlorate the yield of perchlorate is further increased. In the last experiment of series III, the addition of 15 per cent. of powdered quartz to the chlorate resulted in 97 per cent. of the chlorate being decomposed in one and a quarter hours and in 59·3 per cent. of the chlorate being converted into perchlorate. A yield of this amount would therefore involve to some extent a reaction of type (iii).

The results given in Table II show that when a mixture of potassium chlorate and quartz (up to 30 per cent. of the chlorate) is heated in a glass tube, the yield of perchlorate is increased. Further addition of quartz, whilst not affecting the total decomposition, continuously reduces the yield of perchlorate. The amount of free chlorine liberated was very small except in those experiments in which potassium pyrosulphate, and to a lesser extent potassium dichromate, was used.

EXPERIMENTAL.

The silver oxide, prepared from a solution of pure silver nitrate by precipitation with a solution of pure potassium hydroxide, was thoroughly washed and dried. All other substances employed were supplied as pure, but where possible were twice recrystallised before use.

The reaction vessels were tubes 12—15 cm. long and 2 cm. wide. The tubes containing the reaction mixture were heated in an air-furnace, the tube being inserted to about half its length into the furnace. The gases evolved were first passed through a small wash-bottle containing potassium iodide solution. In experiments in which the volume of oxygen was small, the volume was measured directly in a gas burette; in other cases, it was measured by the water-displacement method.

A series of preliminary experiments confirmed Mathers and Aldred's observation (*loc. cit.*) that similar results were obtained for temperatures between 480° and 550°, the period of heating required being determined by the temperature of the experiment.

For each experiment 2 grams of the purified potassium chlorate were intimately mixed with 0·3 gram of the catalyst. The heating was continued until there was no further evolution of gas and no apparent change taking place.

Three types of reaction tube were used: (*a*) an ordinary hard glass tube, (*b*) an unglazed porcelain tube, and (*c*) a quartz tube.

At the end of the experiment the reaction product was thoroughly extracted from the tube by boiling water; and the solution filtered if necessary and made up to 250 c.c. The amount of chloride, chlorate, and perchlorate, respectively, was determined by the method described in Treadwell and Hall's "Analytical Chemistry" (Vol. II, pp. 461—464, 4th ed., 1915), the chlorate being reduced by the ferrous sulphate method and the perchlorate by ignition with ammonium chloride. From the results obtained, the total amount of each salt was calculated.

In the majority of the experiments the potassium iodide solution became coloured; but in most cases the amount of iodine liberated was very small. In order, however, to obtain some idea of the relative amounts of chlorine liberated, the iodine was estimated by titration with $N/500$-thiosulphate solution; the values obtained are given in Table I, col. 5.

The results are given in Table I, the chloride and perchlorate being expressed in terms of chlorate converted. The reaction tubes are of glass, unglazed porcelain, and quartz in series I, II, and III, respectively.

The results of a series of experiments in which mixtures of potassium chlorate with various amounts of powdered quartz were heated in glass reaction tubes are given in Table II.

TABLE I.

Series I. Glass reaction tube.

Catalyst employed.	Temp.	Period of heating (mins.).	Grams of oxygen per 100 grams of chlorate.	Grams of free chlorine per 100 grams of chlorate.	Percentage of unchanged chlorate.	Percentage of chlorate converted into chloride.	Percentage of chlorate converted into perchlorate.
None	540°	45	11·612	0·005	15·030	43·591	41·134
Silver oxide	280	120	0·745	nil	99·865	trace	nil
Silver oxide	350	,,	1·032	nil	99·895	trace	nil
Silver oxide	380	,,	21·360	0·045	46·290	52·180	1·212
Potassium chloride	540	30	13·622	0·030	9·605	48·462	41·363
Aluminium silicate	540	,,	19·176	0·060	33·855	53·501	13·574
Potassium sulphate	540	,,	13·976	0·050	8·690	49·213	41·650
Potassium pyrosulphate	510	75	16·340	3·545	7·400	45·863	39·291
Potassium dichromate	510	,,	18·198	0·265	27·700	51·520	20·232
Thorium oxide	510	,,	39·140	nil	0·195	99·791	nil
Zirconium oxide	510	60	19·310	0·010	6·650	62·163	31·120
Cerium oxide	510	,,	38·981	0·005	0·660	99·281	nil
Powdered glass	510	75	27·162	0·010	3·400	76·402	20·261
Powdered porcelain	510	,,	15·071	0·025	4·255	52·661	43·000
Powdered quartz	510	,,	13·850	nil	3·410	50·634	45·981

Series II. Unglazed porcelain reaction tube.

None	510°	90	11·612	0·006	14·640	43·460	41·590
Silver oxide	280	120	0·738	nil	99·855	trace	nil
Silver oxide	350	,,	1·139	0·005	99·895	trace	nil
Silver oxide	380	,,	20·878	0·030	46·835	52·672	1·522
Potassium chloride	510	60	13·659	0·005	9·575	48·771	41·581
Aluminium silicate	510	,,	18·738	0·035	32·250	53·212	14·201
Potassium sulphate	510	,,	14·242	0·025	7·515	50·490	41·852
Potassium pyrosulphate	500	75	17·031	3·545	7·085	44·713	40·690
Potassium dichromate	500	,,	18·084	0·262	27·550	51·870	20·037
Thorium oxide	500	,,	39·102	nil	0·345	99·530	nil
Zirconium oxide	500	,,	19·510	0·01	6·305	61·732	31·802
Cerium oxide	500	,,	38·721	0·005	1·340	98·581	nil
Powdered glass	500	,,	26·703	0·05	4·592	74·854	20·500
Powdered porcelain	500	,,	14·592	0·02	3·950	51·822	44·081
Powdered quartz	500	,,	13·364	nil	3·625	49·631	46·663

TABLE I (*continued*).

Series III. Quartz reaction tube.

Catalyst employed.	Temp.	Period of heating (mins.).	Grams of oxygen per 100 grams of chlorate.	Grams of free chlorine per 100 grams of chlorate.	Percentage of unchanged chlorate.	Percentage of chlorate converted into chloride.	Percentage of chlorate converted into perchlorate.
None	480°	60	9·190	0·01	9·965	40·201	49·780
Silver oxide	280	120	1·229	nil	99·831	trace	nil
Silver oxide	350	,,	1·455	0·01	95·615	2·371	1·697
Silver oxide	380	,,	20·761	0·03	46·660	51·112	1·990
Potassium chloride	480	60	9·498	0·035	8·332	41·260	50·371
Aluminium silicate	480	,,	17·421	0·135	31·335	50·443	18·193
Potassium sulphate	480	,,	10·510	0·01	3·991	44·162	52·042
Potassium pyrosulphate	500	75	12·731	4·065	8·652	35·234	47·961
Potassium dichromate	500	,,	16·632	0·23	26·241	49·635	23·470
Thorium oxide	500	,,	38·320	nil	1·490	97·903	0·610
Zirconium oxide	500	,,	19·241	0·01	5·912	60·260	33·712
Cerium oxide	500	,,	38·700	nil	1·225	98·721	nil
Powdered glass	500	,,	22·480	nil	4·500	66·971	28·451
Powdered porcelain	500	,,	8·705	0·02	3·835	40·442	54·892
Powdered quartz	500	,,	6·821	nil	3·100	36·981	59·294

TABLE II.

Temperature 510°. Period of heating 1 hr. 15 mins.

Grams of quartz per 100 grams of chlorate.	Grams of oxygen per 100 grams of chlorate.	Grams of chlorine per 100 grams of chlorate.	Percentage of unchanged chlorate.	Percentage of chlorate as chloride.	Percentage of chlorate as perchlorate.
15	13·848	nil	3·410	50·634	45·981
30	10·624	0·005	3·915	44·332	51·760
40	12·154	0·005	4·180	47·221	48·552
50	14·132	0·005	3·580	51·170	45·215
75	14·271	0·015	3·625	51·342	44·892
100	15·476	0·025	3·675	53·491	42·871

Summary.

1. The yield of potassium perchlorate obtained by heating the chlorate is not increased by the addition of silver oxide, the whole of the silver oxide being decomposed before any appreciable amount of perchlorate is formed.

2. The yield of perchlorate is influenced by the nature of the reaction vessel, being greatest for quartz vessels.

3. When a mixture of potassium chlorate with 15 per cent. of powdered quartz was heated in a quartz tube, 59·3 per cent. of the chlorate was converted into perchlorate and 3 per cent. was unchanged.

4. The addition of cerium and thorium oxides results in almost complete decomposition of the chlorate into chloride and oxygen, whilst zirconium oxide and glass considerably reduce the yield of perchlorate, but increase the yield of chloride and oxygen. Aluminium silicate and potassium dichromate considerably reduce the percentage of chlorate decomposed.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, August 3rd*, 1923.]

XII.—*The Additive Formation of Four-membered Rings. Part III. The Nomenclature of Four-membered Heterocyclic Rings, and the Formation and Properties of some Derivatives of Methylene-1 : 2 : 4-oxadi-imine.*

By CHRISTOPHER KELK INGOLD.

IN two concurrent series of investigations, one entitled the "Chemistry of Polycyclic Structures" and the other the "Structure of the Benzene Nucleus," evidence is being brought forward that the chemistry of derivatives of (*a*) *cyclo*pentadiene, (*b*) benzene is to be referred to intra-annular changes of the following type :

The changes that occur in these systems must find their counterpart in heterocyclic systems such as thiophen and pyridine, and although, for a reason given below, the study of these heterocyclic systems is being postponed, the interpretation which it has been sought to place on the characteristics of the homocyclic rings must stand or fall by the possibility of its general application throughout the whole of aromatic-heterocyclic chemistry.

Thus we are led to the view, first, that the tautomeric change

must be a process having great generality, and, secondly, that since the tendency, which this change implies, towards the interaction of the two unsaturated residues, W:X and Y:Z, "must operate no matter whether they are in the same or in different molecules, each type of tautomeric change will have its counterpart in a reversible additive process" (Usherwood, T., 1923, **123**, 1719). Hence one

of the objects of these investigations is the establishment of the generality of the reversible additive process, the intermolecular analogue of the tautomeric change referred to, for all the commoner types of double linking :

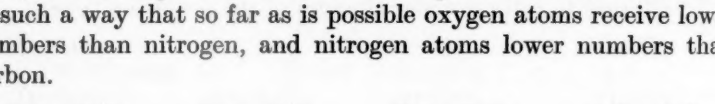
In a preliminary survey of the subject the generality of the change has been thoroughly established for the groups C:C, C:N, C:O, N:N, and N:O.

Examples of most of the expected new types of four-membered ring have already been obtained, and the variety of new heterocyclic rings which it appears possible to produce by this method of ring formation, hitherto largely neglected, is such as to necessitate a definite scheme for the nomenclature of these compounds.

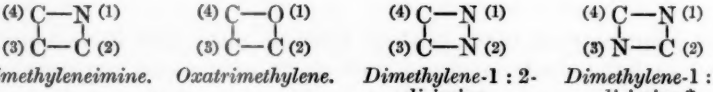
The scheme proposed is derived by application of the following two rules.

(i) The name.—The groups or atoms CH_2, O, S, and NH in the unsubstituted and fully hydrogenated ring are denoted by methylene, oxa, thia, and imine respectively.

(ii) Numbering.—The atoms of the ring are numbered in rotation in such a way that so far as is possible oxygen atoms receive lower numbers than nitrogen, and nitrogen atoms lower numbers than carbon.

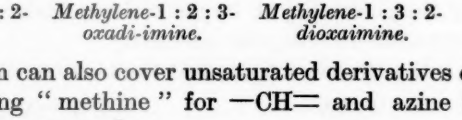


Trimethyleneimine. *Oxatrimethylene.* *Dimethylene-1 : 2-di-imine.* *Dimethylene-1 : 3-di-imine.**



Dimethylene-1 : 2-oxaimine. *Methylene-1 : 2 : 3-oxadi-imine.* *Methylene-1 : 3 : 2-dioxaimine.* *1 : 3-Dioxadi-imine.*

The system can also cover unsaturated derivatives of any of these rings by using " methine " for —CH= and azine for —N=, as in the following examples :



Dimethine-1 : 3-diazine. *Methine-1 : 2 : 4-thiaimineazine.*

One of the objects with which these investigations were commenced arose in connexion with the relation which these additive

* In Parts I and II of this series this ring was termed " dimethinediazidine " from its relation to the unsaturated ring dimethinediazine.

reactions bear to the intra-nuclear tautomeric changes mentioned above. Since intermolecular reactions are usually more easily amenable to experimental treatment than mobile tautomeric changes, it was hoped that a preliminary study of the additive process might yield some indication, to guide the study of the tautomerism within the aromatic heterocyclic nuclei, as to which nuclei are likely to possess the most stable bridged phases involving four-membered rings. From this point of view the production of an unusually stable four-membered ring is a matter of some interest.

It has been shown (Ingold and Piggott, T., 1922, **121**, 2381; 1923, **123**, 2745) that the stability of dimethylene-1 : 3-di-imines (diazidines) varies greatly with the combined bulk of the substituent groups, a certain optimum of substitution corresponding with maximal stability. This optimum is approximately attained in the case of the ditolyl compound (II), which is stable at the ordinary temperature, although the equilibrium with the azomethine (I) gradually shifts over on heating and is in favour of the latter at 250°.

(I. *Stable at higher temperatures.*) $CH_2{:}N{\cdot}C_7H_7 \rightleftharpoons \begin{matrix} CH_2{\cdot}N{\cdot}C_7H_7 \\ | \\ C_7H_7{\cdot}N{-}CH_2 \end{matrix}$ (II. *Stable in the cold.*)

It has for long been believed, and new experiments confirming this point will shortly be published, that the same type of general relationship holds for nitroso-compounds and dioxadi-imines. Here, the optimum of substitution is approximately attained in the case of the simpler derivatives of nitrosobenzene (III), the dioxadi-imines (IV) being the more stable at or below the ordinary temperature :

(III. *Stable at higher temperatures.*) $O{:}NAr \rightleftharpoons \begin{matrix} O{-}NAr \\ | \\ ArN{-}O \end{matrix}$ (IV. *Stable in the cold.*)

It therefore seemed probable that if a nitroso-compound and an azomethine, each chosen from the class within its respective group known to possess a strong tendency towards the formation of four-membered rings, were placed together, additive union would occur, and an unusually stable four-membered ring might result.

Experiment has shown this to be the case. Azomethines of type (I) and nitroso-compounds of type (III) react with remarkable ease, at the ordinary temperature and in the absence of any condensing agent, giving a series of well crystallised, four-membered ring compounds, eight of which are described in the experimental portion of this paper.

Two constitutions (V and VI) are possible for a four-membered ring produced in the manner described.

(V.) $\begin{matrix} ArN{-}O \\ | \\ Ar'N{-}CH_2 \end{matrix}$ $\qquad$ $\begin{matrix} ArN{-}O \\ | \\ H_2C{-}NAr' \end{matrix}$ (VI.)

In either case, thermal division might regenerate the original pair of compounds (VII), and it might also produce the pair (VIII) or (IX) according as the constitution of the substance is represented by (V) or (VI).

$$\underset{\text{(VII.)}}{ArN{:}O + Ar'N{:}CH_2} \qquad \underset{\text{(VIII.)}}{ArN{:}NAr' + CH_2{:}O} \qquad \underset{\text{(IX.)}}{Ar'N{:}O + ArN{:}CH_2}$$

In no case, however, has an azo-compound or formaldehyde been detected amongst the products of thermal division, whilst mixtures of nitroso-compounds were obtained in certain cases; the corresponding azomethines were not isolated, but this is doubtless due to the fact that these two-fold divisions are by no means the principal reactions which set in when the cyclic substances decompose.

This evidence in favour of (VI) is supported by the nature of the products of the principal one of the five or more changes which take place simultaneously with thermal division. In every case investigated, the main product of the decomposition was a carbodi-imide (X), containing the chain N·C·N, water having apparently split off across the four-membered ring in (VI). The structures of the carbodi-imides are readily demonstrated by hydrolytic conversion into carbamides of type (XI), which can be synthesised from the appropriate carbimide and amine. In the course of the decomposition of the four-membered rings, it is usually impossible to prevent a certain proportion of the carbodi-imides from uniting with part of the water originally eliminated, thus giving a certain quantity of the same carbamide which is better prepared by deliberate hydration of the isolated di-imide.

$$\underset{\text{(X.)}}{Ar{\cdot}N{:}C{:}NAr'} \qquad\qquad Ar{\cdot}NH{\cdot}CO{\cdot}NHAr' \ \text{(XI.)}$$

Not only the main reaction, but also all the side reactions which have been encountered agree in a very satisfactory manner with the structure (VI) assigned to the ring compounds. Thus in several cases two carbylamines and two primary amines were identified, evidently arising from the following two-fold decomposition of the structure (VI) :

$$\text{(XII.)} \quad ArN{:}C + NH_2Ar' \longleftarrow \text{(VI.)} \longrightarrow ArNH_2 + C{:}NAr' \quad \text{(XIII.)}$$

Two new carbylamines, p-*chlorophenylcarbylamine* and p-*bromophenylcarbylamine*, were isolated in the course of these experiments as beautifully crystalline solids. They have all the well-known characteristics of carbylamines, including odour and ready hydrolysis by mineral acids. Subsequently, they were synthesised for comparison by the action of chloroform and alcoholic potassium hydroxide on the appropriate primary bases.

The following is a tabular summary showing the actual evidence

on which the above brief statement as to the modes of decomposition of the ring compounds is based :

$$(p)C_6H_4Me\cdot N<\begin{matrix}CH_2\\O\end{matrix}>NPh \quad \text{(XIV.)}$$

Products.	Identification.
$(p)C_6H_4Me\cdot N:C:NPh$ (XV)	Analysis and conversion into carbamide.
$(p)C_6H_4Me\cdot NH\cdot CO\cdot NHPh$ (XVI)	Analysis and preparation from PhN:CO and $C_7H_7\cdot NH_2$.
$(p)C_6H_4Me\cdot N:C$ (XVII) PhN:C (XVIII)	Converted together into amines by hydrolysis, and the amines acetylated and then separated and identified.
$(p)C_6H_4Me\cdot NH_2$ (XIX) $PhNH_2$ (XX)	Acetylated and acetyl derivatives separated and identified.
$(p)C_6H_4Me\cdot N:O$ (XXI) PhN:O (XXII)	Mixture condensed with aniline and the azo-compounds $PhN:N\cdot C_6H_4Me(p)$ and PhN:NPh separated and identified.

$$(p)C_6H_4Cl\cdot N<\begin{matrix}CH_2\\O\end{matrix}>NPh \quad \text{(XXIII).}$$

$(p)C_6H_4Cl\cdot N:C:NPh$ (XXIV)	Like (XV).
$(p)C_6H_4Cl\cdot NH\cdot CO\cdot NHPh$ (XXV)	Analysis and preparation from PhN:C:O and $C_6H_4Cl\cdot NH_2$.
$(p)C_6H_4Cl\cdot N:C$ (XXVI)	Obtained crystalline. Also prepared from $C_6H_4Cl\cdot NH_2$, $CHCl_3$, and KOH.
PhN:C	Hydrolysis to aniline and acetylation.
$(p)C_6H_4Cl\cdot NH_2$ (XXVII) $PhNH_2$	Like (XIX) and (XX), above.

Nitroso-compounds also present.

$$(p)C_6H_4Br\cdot N<\begin{matrix}CH_2\\O\end{matrix}>NPh \quad \text{(XXVIII.)}$$

$(p)C_6H_4Br\cdot N:C:NPh$ (XXIX)	Like (XV).
$(p)C_6H_4Br\cdot NH\cdot CO\cdot NHPh$ (XXX)	Analysis and preparation from PhNCO and $C_6H_4Br\cdot NH_2$.
$(p)C_6H_4Br\cdot N:C$ (XXXI)	Obtained crystalline. Also prepared from $C_6H_4Br\cdot NH_2$, $CHCl_3$, and KOH.
PhN:C	As above.
$(p)C_6H_4Br\cdot NH_2$ (XXXII)	Obtained crystalline. Also like (XIX) and (XX).
$PhNH_2$	Like (XIX) and (XX).
$(p)C_6H_4Br\cdot N:O$ (XXXIII) $C_6H_5\cdot N:O$	Like (XXI) and (XXII). $C_6H_4Br\cdot N:NPh$ fully identified, but PhN:NPh somewhat doubtful.

$$(p)C_6H_4Me\cdot N<\begin{matrix}CH_2\\O\end{matrix}>N\cdot C_6H_4Cl(p) \quad \text{(XXXIV.)}$$

$(p)C_6H_4Me\cdot N:C:N\cdot C_6H_4Cl(p)$ (XXXV)	Like (XV).
$(p)C_6H_4Me\cdot NH\cdot CO\cdot NH\cdot C_6H_4Cl(p)$ (XXXVI)	Analysis and preparation from $C_6H_4Me\cdot N:CO$ and $C_6H_4Cl\cdot NH_2$.
$(p)C_6H_4Cl\cdot N:C$	Obtained crystalline as above.
$(p)C_6H_4Me\cdot N:C$ (XXXVII)	Hydrolysed to *p*-toluidine and acetylated.
$(p)C_6H_4Cl\cdot NH_2$ $(p)C_6H_4Me\cdot NH_2$	Like (XIX) and (XX).

Nitroso-compounds also present.

$$(p)C_6H_4Me\cdot N<\begin{matrix}CH_2\\O\end{matrix}>N\cdot C_6H_4Br(p) \quad \text{(XXXVIII.)}$$

$(p)C_6H_4Me\cdot N{:}C{:}N\cdot C_6H_4Br(p)$ (XXXIX)	Like (XV).
$(p)C_6H_4Me\cdot NH\cdot CO\cdot NH\cdot C_6H_4Br(p)$ (XL)	Analysis and preparation from $C_6H_4Me\cdot NCO$ and $C_6H_4Br\cdot NH_2$.
$(p)C_6H_4Br\cdot N{:}C$	Obtained crystalline as above.
$(p)C_6H_4Me\cdot N{:}C$	Like (XXXVII) above.
$(p)C_6H_4Br\cdot NH_2$)	Like (XIX) and (XX).
$(p)C_6H_4Me\cdot NH_2$)	

Nitroso-compounds also present.

$$(p)C_6H_4Cl\cdot N<\begin{matrix}CH_2\\O\end{matrix}>N\cdot C_6H_4Cl(p) \quad \text{(XLI.)}$$

$(p)C_6H_4Cl\cdot N{:}C{:}N\cdot C_6H_4Cl(p)$ (XLII)	Like (XV).
$(p)C_6H_4Cl\cdot NH\cdot CO\cdot NH\cdot C_6H_4Cl(p)$ (XLIII)	Analysis and comparison of properties.
$(p)C_6H_4Cl\cdot N{:}C$	As above; obtained crystalline.
$(p)C_6H_4Cl\cdot NH_2$	As above; obtained crystalline.
$(p)C_6H_4Cl\cdot N{:}O$	Condensed with aniline to give $C_6H_4Cl\cdot N{:}NPh$.

$$(p)C_6H_4Br\cdot N<\begin{matrix}CH_2\\O\end{matrix}>C_6H_4Br(p) \quad \text{(XLIV.)}$$

$(p)C_6H_4Br\cdot N{:}C{:}N\cdot C_6H_4Br(p)$ (XLV)	Like (XV).
$(p)C_6H_4Br\cdot NH\cdot CO\cdot NH\cdot C_6H_4Br(p)$ (XLVI)	Analysis and comparison of properties.
$(p)C_6H_4Br\cdot N{:}C$	As above; obtained crystalline.
$(p)C_6H_4Br\cdot NH_2$	As above; obtained crystalline.
$(p)C_6H_4Br\cdot N{:}O$	Obtained crystalline; also condensed with aniline to give $C_6H_4Br\cdot N{:}NPh$.

$$(p)C_6H_4Br\cdot N<\begin{matrix}CH_2\\O\end{matrix}>C_6H_4Cl(p) \quad \text{(XLVII.)}$$

$(p)C_6H_4Br\cdot N{:}C{:}N\cdot C_6H_4Cl$ (XLVIII)	Like (XV).
$(p)C_6H_4Br\cdot NH\cdot CO\cdot NH\cdot C_6H_4Cl$ (XLIX)	Analysis.

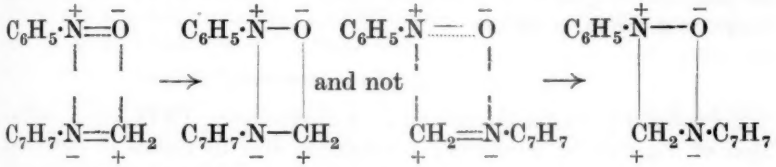
Carbylamines, primary amines, and nitroso-compounds also present.

These experiments afford strong presumptive evidence in favour of (VI) and a complete disproof of (V), but the former constitution is not conclusively proved, because it is possible, although somewhat improbable, that a substance of formula (VI), originally formed, undergoes subsequent rearrangement :

$$\text{(VI.)} \longrightarrow ArNH\cdot CH<\begin{matrix}O\\ \\ \end{matrix}NAr' \text{ (L.)} \longrightarrow ArNH\cdot CH{:}\overset{O}{\underset{|}{N}}Ar' \text{ (LI.)}$$

This possibility was eliminated as follows. Of the formulæ (V), (VI), (L), and (LI), the second is unique in the respect that the two aromatic nuclei occupy corresponding positions in the molecule, so that if Ar and Ar′ be interchanged the substance will remain the same; in other words, a substance having this formula will be obtained, not only from $ArN{:}O$ and $Ar'N{:}CH_2$, but also from $Ar'N{:}O$ and $ArN{:}CH_2$. This proved to be the case.

The establishment of this formula provides an interesting test of the hypothesis by means of which so many obscure points of chemistry are nowadays "explained." In nitrosobenzene oxygen is the "key" atom (Lapworth, T., 1922, **121**, 416), and the compound may be represented as $C_6H_5—\overset{+}{N}=\overset{-}{O}$. In methylenetoluidine nitrogen is the "key" atom, and the formula is $C_7H_7—\overset{-}{N}=\overset{+}{C}H_2$, a disposition of signs which, it would doubtless be claimed, is confirmed by the behaviour of the substance (and the whole class to which it belongs) on hydrolysis. Hence, if the two double linkings depicted above enter into additive union, they must yield



which is totally contrary to the facts of the case.

Experimental.

Methylene-*p*-toluidine was prepared by the method already described (T., 1923, **123**, 2745).

Methylene-p-*chloroaniline*, $CH_2{:}N{\cdot}C_6H_4Cl$.—The crystalline product obtained by keeping a mixture of 50 c.c. of 40 per cent. formaldehyde with 200 c.c. of an alcoholic solution of *p*-chloroaniline (70 grams) for twelve hours was collected, washed with a little absolute alcohol, and recrystallised from petroleum (b. p. 100—120°), from which it separated in long needles, m. p. 142° (Found: C = 60·3; H = 4·3. C_7H_6NCl requires C = 60·2; H = 4·3 per cent.). The yield was 60 per cent.

Methylene-p-*bromoaniline*, $CH_2{:}N{\cdot}C_6H_4Br$.—Prepared from 250 c.c. of an alcoholic solution of 90 grams of *p*-bromoaniline as in the preceding case, this substance formed a colourless mass of very long, felted needles resembling glass wool, m. p. 169° (Found: C = 45·9; H = 3·4. C_7H_6NBr requires C = 45·7; H = 3·3 per cent.). The yield was 60 per cent.

All three methylene bases are readily soluble in cold alcohol or chloroform, but sparingly soluble in cold benzene or light petroleum.

p-*Chloronitrosobenzene*.—Finely ground ammonium persulphate (290 grams) was added to 170 c.c. of cold concentrated sulphuric acid during one hour, care being taken to avoid any rise of temperature. After a further fifteen minutes, the solution was poured on to 1500 c.c. of ice and water, the solution neutralised with solid

sodium carbonate below 5°, 60 grams of finely powdered *p*-chloroaniline were added, and the solution was mechanically stirred for one hour, the temperature being maintained at 0—5° and the solution kept as nearly neutral as possible by the addition of sodium carbonate solution. The brown precipitate was then collected, triturated with water to remove salts, and then with *N*-hydrochloric acid to remove unchanged base, and distilled with steam. The nitroso-compound, which solidified in the distillate, was crystallised from ethyl alcohol. The yield was 25 grams, and the m. p. 90°.

p-*Bromonitrosobenzene*.—This was prepared exactly like the chloro-compound excepting that 80 grams of *p*-bromoaniline were employed in place of 60 grams of *p*-chloroaniline. The yield was about the same, and the m. p. 94°.

Formation of the Four-membered Rings.

2-*Phenyl*-4-p-*tolylmethylene*-1 : 2 : 4-*oxadi-imine* (XIV).—A solution of 5 grams of methylene-*p*-toluidine and 10 grams of nitrosobenzene in a minimum of cold chloroform was kept at the ordinary temperature for forty hours, the solvent allowed to evaporate, and the residue washed with small quantities of benzene until the washings were no longer blue. The crude product was recrystallised from boiling benzene, from which it separated in colourless needles, m .p. 150°. The yield of the purified substance was 6 grams (Found : C = 74·1; H = 6·4; N = 12·6. $C_{14}H_{14}ON_2$ requires C = 74·3; H = 6·2; N = 12·4 per cent.).

It is desirable in this and in the following additive reactions to use an excess of nitroso-compound in order to bring into reaction the last traces of azomethine, which otherwise interferes with the purification of the ring-compound. The time for which the reaction mixture should be kept should be just sufficient to ensure the destruction of the azomethine, and this is best determined by examining test samples from time to time, as the necessary period depends on the atmospheric temperature. If too long a time is allowed, the excess of nitrosobenzenes will undergo other decompositions, particularly in daylight, forming azoxybenzenes and other products which also interfere with the purification, and so cause a diminution in the ultimate yield. The oil washed out by cold benzene from the crude product of the above additive reaction yielded on distillation a fraction, b. p. 200—205°/11 mm., which solidified on cooling. The solid was identified as azoxybenzene by direct comparison and by reduction to azobenzene.

2-*Phenyl*-4-p-*chlorophenylmethylene*-1 : 2 : 4-*oxadi-imine* (XXXIII).—Five grams of methylene-*p*-chloroaniline and 7·5 grams of nitrosobenzene dissolved in chloroform were kept for seventy hours, and the

product was then isolated as in the preceding instance and crystallised from benzene. It separated in long, colourless needles, m. p. 162° (Found : C = 63·1; H = 4·7. $C_{13}H_{11}ON_2Cl$ requires C = 63·3; H = 4·5 per cent.).

2-*Phenyl*-4-p-*bromophenylmethylene*-1 : 2 : 4-*oxadi-imine* (XXVIII).—A solution of 5 grams of methylene-*p*-bromoaniline and 6 grams of nitrosobenzene in 75 c.c. of chloroform was kept for fifty-four hours, and the crystalline product collected. The liquid was then allowed to evaporate at the ordinary temperature, and the crystals which separated were collected from time to time. The ultimate residue set to a paste, which was drained on porous porcelain and washed with benzene. The combined crops of crystals were recrystallised from boiling benzene, from which colourless, felted needles separated, m. p. 171° (Found : C = 53·5; H = 3·9. $C_{13}H_{11}ON_2Br$ requires C = 53·6; H = 3·8 per cent.).

4-p-*Chlorophenyl*-2-p-*tolylmethylene*-1 : 2 : 4-*oxadi-imine* (XXXIV).—This compound was prepared similarly from 4 grams of methylene-*p*-toluidine and 8 grams of *p*-chloronitrosobenzene. It separated from benzene in silky needles, m. p. 163° (Found : C = 64·5; H = 5·1. $C_{14}H_{13}ON_2Cl$ requires C = 64·5; H = 5·0 per cent.).

4-p-*Bromophenyl*-2-p-*tolylmethylene*-1 : 2 : 4-*oxadi-imine* (XXXVII).—This was prepared from 4 grams of methylene-*p*-toluidine and 10 grams of *p*-bromonitrosobenzene. The product was isolated as in the case of compound (XXVII) and crystallised from benzene, from which it separated in felted needles, m. p. 158° (Found : C = 55·1; H = 4·3. $C_{14}H_{13}ON_2Br$ requires C = 55·1; H = 4·3 per cent.).

2 : 4-*Di*-p-*chlorophenylmethylene*-1 : 2 : 4-*oxadi-imine* (XLI) was prepared from 4 grams of methylene-*p*-chloroaniline and 8·5 grams of *p*-chloronitrosobenzene. It separated from benzene in silky needles, m. p. 171° (Found : C = 55·9; H = 3·8. $C_{13}H_{10}ON_2Cl_2$ requires C = 55·5; H = 3·5 per cent.).

2 : 4-*Di*-p-*bromophenylmethylene*-1 : 2 : 4-*oxadi-imine* (XLIV) was obtained from 4 grams of methylene-*p*-bromoaniline and 7·5 grams of *p*-bromonitrosobenzene. It crystallised from much benzene in rosettes of silky needles, m. p. 175° (Found : C = 42·6; H = 2·9. $C_{13}H_{10}ON_2Br_2$ requires C = 42·2; H = 2·7 per cent.).

Decomposition of the Ring Compounds by Heat.

Each of these decompositions was carried out in a specially blown bulb furnished with a delivery tube containing three bulbs, each of which could be heated with steam or cooled with water independently of the others. The substance to be decomposed was heated

in the decomposition-bulb in a sulphuric-acid bath at 170° at atmospheric pressure while all three receiving bulbs were jacketed with steam. The second and third bulbs were then jacketed with cold water, and the first with steam, the apparatus was evacuated, and the products of decomposition were cautiously distilled over. After a little practice it was an easy matter to adjust the rate of distillation so that the first receiving bulb caught the whole of the carbodi-imide and carbamide, whilst the other two bulbs received the more volatile products. The apparatus was then cut up and the contents of each bulb were investigated separately.

(a) *Products from* 2-*Phenyl*-4-p-*tolylmethylene*-1 : 2 : 4-*oxadi-imine* (XIV).

Phenyl-p-*tolylcarbodi-imide* (XV).—The product in the first bulb was mixed with cold absolute alcohol and filtered. The filtrate was evaporated under reduced pressure and the residue redistilled, when a pale yellow, glassy distillate was obtained, b. p. 170°/12 mm. (Found: C = 80·2; H = 5·8. $C_{14}H_{12}N_2$ requires C = 80·8; H = 5·8 per cent.). On boiling with water or allowing to stand in contact with aqueous-alcoholic hydrochloric acid, this substance is converted into the carbamide described below.

Phenyl-p-*tolylcarbamide* (XVI).—The residue from the alcoholic solution (above) was crystallised from glacial acetic acid, from which pearly leaflets separated, m. p. 218°. This substance, which was also obtained by hydration of the di-imide, was identified by analysis (Found: C = 74·2; H = 6·5. Calc., C = 74·3; H = 6·2 per cent.) and by comparison with an authentic specimen.

Aniline and p-*Toluidine.*—The product in the second and the third bulb smelt strongly of carbylamines. It was mixed with cold dilute hydrochloric acid and extracted with ether. The aqueous layer was made alkaline with sodium hydroxide and the bases were recovered and acetylated in the usual manner. Aceto-*p*-toluidide, m. p. 150°, was readily obtained by fractional crystallisation from dilute alcohol (Found: C = 72·5; H = 7·5. Calc., C = 72·5; H = 7·3 per cent.), whilst from the ultimate mother-liquors a small amount of pure acetanilide was also obtained, m. p. 114°.

Phenylcarbylamine and p-*Tolylcarbylamine.*—The quantity of these substances produced was insufficient to render a complete separation practicable, and therefore they were hydrolysed and the bases identified. The ether extract of neutral products (above) was evaporated and the residue mixed with 2*N*-hydrochloric acid and distilled in steam for about two minutes. The residual liquid was filtered from a trace of tar, made alkaline, and the bases were

collected, acetylated, and identified through their acetyl derivatives as aniline and *p*-toluidine as described above.

Nitrosobenzene and p-*Nitrosotoluene.*—These were collected from the steam distillate. As fractional crystallisation did not appear to lead to a separation, and the product was obviously a mixture, it was dissolved in acetic acid and warmed with aniline. The azo-compounds precipitated on dilution were fractionally crystallised from dilute acetic acid and in this way benzeneazo-*p*-toluene, m. p. 68° (Found : C = 79·6; H = 6·1. Calc., C = 79·6; H = 6·1 per cent.), was separated in the pure condition. A substance was also obtained which did not depress the melting point of azobenzene, but depressed that of benzeneazo-*p*-toluene; the quantity was insufficient for analysis, but the substance was doubtless azobenzene.

(b) *Products from* 2-*Phenyl*-4-p-*chlorophenylmethylene*-1 : 2 : 4-*oxadiimine* (XXIII).

Phenyl-p-*chlorophenylcarbodi-imide* (XXIV).—This substance was collected along with the carbamide, and was isolated as in the preceding instance as a very viscous liquid, b. p. 175°/11 mm. (Found : C = 68·0; H = 4·2. $C_{13}H_9N_2Cl$ requires C = 68·3; H = 4·0 per cent.). On hydration, it yields the carbamide.

p-*Chlorodiphenylcarbamide* (XXV) was purified by crystallisation from glacial acetic acid and identified by analysis (Found : C = 63·3; H = 4·8. Calc., C = 63·3; H = 4·5 per cent.), by m. p. (238—242°), and by comparison with a specimen prepared from *p*-chloroaniline and phenylcarbimide.

p-*Chlorophenylcarbylamine* (XXVI).—This carbylamine separated from the more volatile distillate in long needles, and in the first experiment was isolated by draining on porous porcelain. It is, however, better first to separate the bases as described in the preceding experiment. By crystallisation from a small amount of dry ether the compound was obtained in long needles, m. p. 71°, which turned brown on exposure to air (Found : C = 61·2; H = 2·9. C_7H_4NCl requires C = 61·1; H = 2·9 per cent.).

This carbylamine has not been described previously and therefore it was prepared for comparison by the following method : *p*-Chloroaniline (27 grams), dissolved in 43 c.c. of chloroform, was added little by little and with shaking to a solution of 48 grams of potassium hydroxide in 160 c.c. of alcohol, the temperature being maintained at 50—60°. After a further fifteen minutes the alcohol was evaporated on the steam-bath, and water (200 c.c.) added. The oil was extracted with ether and the extract rapidly washed with 25 c.c. of concentrated hydrochloric acid diluted with 200 c.c. of water. The

solid which separated (probably the hydrochloride of a formamidine) was removed, and the ether extract washed a few more times with water, and then dried by shaking with solid potassium hydroxide, until no more precipitate separated. The filtered solution was evaporated to small bulk, again shaken with potassium hydroxide, filtered, and then completely evaporated. The crystalline residue was drained and then crystallised from dry ether, from which long needles, m. p. 71°, separated. The compound has a somewhat less powerful odour than phenylcarbylamine itself, but the taste of the vapour is considerably stronger. On hydrolysis with dilute hydrochloric acid it yields formic acid and *p*-chloroaniline.

Phenylcarbylamine was not isolated as such, but its presence in the liquid portion of the carbylamine fraction was proved by hydrolysis and subsequent acetylation. The ultimate product was a mixture of *p*-chloroacetanilide and acetanilide, from which the latter was separated in a pure condition (Found : C = 71·0; H = 6·9. Calc., C = 71·1; H = 6·7 per cent.).

Aniline and p-*Chloroaniline.*—These were isolated and separated in the form of their acetyl derivatives as in the previous instance (Found : for *p*-chloroacetanilide, C = 56·3; H = 4·7. Calc., C = 56·6; H = 4·7 per cent.).

Nitroso-compounds were detected qualitatively, but not separated.

(c) *Products from* 4-p-*Bromophenyl-2-phenylmethylene*-1 : 2 : 4-*oxadiimine* (XXVIII).

p-*Bromodiphenylcarbodi-imide* (XXIX).—This substance was isolated like its analogues and obtained as a viscous liquid, b. p. 185°/11 mm. (Found : C = 56·7; H = 3·5. $C_{13}H_9N_2Br$ requires C = 57·1; H = 3·3 per cent.). On hydration by means of aqueous-alcoholic hydrochloric acid it yields the carbamide.

p-*Bromodiphenylcarbamide* (XXX) was crystallised from glacial acetic acid and identified by analysis (Found : C = 53·5; H = 4·0. $C_{13}H_{11}ON_2Br$ requires C = 53·6; H = 3·8 per cent.), m. p. (235—250°), and comparison with a specimen prepared from *p*-bromoaniline and phenylcarbimide.

p-*Bromophenylcarbylamine* (XXXI).—This beautifully crystalline carbylamine, m. p. 99°, was isolated and purified like the chlorocarbylamine (Found : C = 46·3; H = 2·3. C_7H_4NBr requires C = 46·1; H = 2·2 per cent.). It was also prepared from *p*-bromoaniline, chloroform, and alcoholic potassium hydroxide by the method used in the case of the chlorocarbylamine (37 grams of *p*-bromoaniline were employed, the other quantities being as stated above). On hydrolysis by dilute hydrochloric acid it yielded

formic acid and *p*-bromoaniline. Its odour and taste closely resemble those of the chloro-compound.

Phenylcarbylamine was identified as in the preceding instance (Found: for acetanilide, C = 71·0; H = 6·8. Calc., C = 71·1; H = 6·7 per cent.).

p-*Bromoaniline*.—The basic fraction, obtained as previously described, partly crystallised, and the crystals were identified as *p*-bromoaniline by direct comparison and a mixed melting-point determination, and also by the m. p. of the acetyl derivative.

Aniline.—The liquid part of the basic fraction contained aniline, which was identified in the form of its acetyl derivative.

Nitrosobenzene and p-*Bromonitrosobenzene*.—These were isolated as in experiment (a). In this case also, fractional crystallisation proved of no avail and therefore the substances were condensed with aniline. The separation of *p*-bromoazobenzene and azobenzene by crystallisation from acetic acid could be followed by the difference in colour of the two azo-compounds, and a pure specimen of the orange bromo-compound, m. p. 89°, was readily obtained (Found: C = 55·4; H = 3·6. Calc., C = 55·2; H = 3·4 per cent.). The azobenzene could not be freed from traces of the bromo-compound and therefore its identity was not completely established.

(d) *Products from* 4-p-*Chlorophenyl*-2-p-*tolylmethylene*-1 : 2 : 4-*oxadiimine* (XXXIV).

p-*Tolyl*-p-*chlorophenylcarbodi-imide* (XXXV).—This substance was isolated like its analogues as a viscous liquid, b. p. 175°/10 mm., and identified by conversion into the carbamide described below.

p-*Chlorophenyl*-p-*tolylcarbamide* (XXXVI).—This was obtained, (i) from the original product of decomposition, (ii) from the carbodiimide by hydration with aqueous-alcoholic hydrochloric acid, and (iii) by the action of *p*-tolylcarbimide on *p*-chloroaniline. The products were purified by crystallisation from glacial acetic acid, from which they separated in large needles, m. p. 297—299° (decomp.), and were identified as the same substance by direct comparison (Found: C = 64·4; H = 5·2. $C_{14}H_{13}ON_2Cl$ requires C = 64·5; H = 5·0 per cent.).

p-*Chlorocarbylamine* was obtained crystalline as in experiment (b).

p-*Tolylcarbylamine* was identified by conversion into acetotoluidide (Found: C = 72·2; H = 7·4. Calc., C = 72·5; H = 7·3 per cent.).

p-*Toluidine and* p-*chloroaniline* were separated as their acetyl derivatives as in the previously described experiments.

Nitroso-compounds were detected qualitatively, but not identified individually.

(e) *Products from* 4-p-*Bromophenyl*-2-p-*tolylmethylene*-1 : 2 : 4-*oxadiimine* (XXXVIII).

p-*Bromophenyl*-p-*tolylcarbodi-imide* (XXXIX) was isolated like its analogues as a pale yellow, viscous liquid, b. p. 188°/10 mm., and was identified by conversion into the carbamide described below.

p-*Bromophenyl*-p-*tolylcarbamide* (XL) was obtained from the original product of the decomposition and from the carbodi-imide and was synthesised for comparison from *p*-tolylcarbimide and *p*-bromoaniline. It separated in needles from much glacial acetic acid, and melted with decomposition at 316—318° (Found: C = 55·2; H = 4·6. $C_{14}H_{13}ON_2Br$ requires C = 55·1; H = 4·3 per cent.).

p-*Tolylcarbylamine and* p-*bromophenylcarbylamine* were isolated and identified as in the preceding experiment (d).

p-*Toluidine and* p-*bromoaniline* were identified as in the preceding experiment, part of the bromoaniline being also isolated in the crystalline condition.

Nitroso-compounds were detected, but not identified individually.

(f) *Products from* 2 : 4-*Di*-p-*chlorophenylmethylene*-1 : 2 : 4-*oxadiimine* (XLI).

pp′-*Dichlorodiphenylcarbodi-imide* (XLII) was isolated as a yellow, very viscous liquid, b. p. 190°/10 mm. (Found: C = 59·8; H = 3·1. $C_{13}H_8N_2Cl_2$ requires C = 59·8; H = 3·1 per cent.). On hydration, it yielded the carbamide described below.

pp′-*Dichlorodiphenylcarbamide* (XLIII), obtained either from the carbodi-imide or the original product of decomposition, was crystallised from glacial acetic acid and identified by analysis (Found: C = 55·6; H = 3·8. $C_{13}H_{10}ON_2Cl_2$ requires C = 55·5; H = 3·5 per cent.), and direct comparison with a genuine specimen.

p-*Chloroaniline.*—The basic fraction of the more volatile distillate readily solidified and was identified as *p*-chloroaniline by direct comparison and a mixed melting-point determination, and also by the m. p. of its acetyl derivative.

p-*Chloronitrosobenzene.*—The steam distillate obtained in the presence of hydrochloric acid gave a nitroso-compound which was identified as *p*-chloronitrosobenzene by its m. p. (89°), by analysis (C = 50·9; H = 2·9. Calc., C = 50·9; H = 2·8 per cent.), and by conversion into *p*-chloroazobenzene.

p-*Chlorophenylcarbylamine* was identified by hydrolysis to *p*-chloroaniline in the first experiment, but it was found subsequently that it could be isolated in the pure condition by cautiously steam-distilling most of the nitroso-compound and then crystallising the less volatile residue from ether.

(g) *Products from* 2 : 4-*Di*-p-*bromophenylmethylene*-1 : 2 : 4-*oxadi-imine* (XLIV).

pp'-*Dibromodiphenylcarbodi-imide* (XLVII) was isolated as a yellow, viscous liquid, b. p. 202°/10 mm., and was identified by conversion into the carbamide.

pp'-*Dibromodiphenylcarbamide* (XLVIII) was prepared, purified, and identified as in the preceding experiment (Found : C = 41·9; H = 3·0. $C_{13}H_{10}ON_2Br_2$ requires C = 42·2; H = 2·7 per cent.).

p-*Bromoaniline* was isolated and identified like the *p*-chloroaniline in the preceding experiment.

p-*Bromonitrosobenzene* was separated by steam distillation with a mineral acid and identified by its m. p. (94°) and analysis (Found : C = 39·0; H = 2·2. Calc., C = 38·9; H = 2·1 per cent.), and also by conversion into *p*-bromoazobenzene.

p-*Bromophenylcarbylamine* was isolated by neutral distillation in steam and crystallisation from ether. It melted at 99° (Found : C = 46·2; H = 2·3. C_7H_4NBr requires C = 46·1; H = 2·2 per cent.).

Proof of Equivalence of the 2- *and* 4-*Positions in Methylene*-1 : 2 : 4-*oxadi-imine.*

2-p-*Chlorophenyl*-4-p-*bromophenylmethylene*-1 : 2 : 4-*oxadi-imine* (XLVII). (a) *Formation from Methylene*-p-*chloroaniline and* p-*Bromonitrosobenzene.*—This reaction was carried out like those previously described, using 2·5 grams of methylene-*p*-chloroaniline and 6 grams of *p*-bromonitrosobenzene. The product separated from benzene in needles, m. p. 171° (Found : C = 47·7; H = 3·2. $C_{13}H_{10}ON_2ClBr$ requires C = 47·9; H = 3·1 per cent.).

(b) *Formation from Methylene*-p-*bromoaniline and* p-*Chloronitrosobenzene.*—The product obtained from 4 grams of methylene-*p*-bromoaniline and 6 grams of *p*-chloronitrosobenzene melted at 171° and was identical in all respects with the substance obtained by the preceding method.

On heating above the melting point, the substance decomposes, yielding a series of products generally analogous to those previously encountered (above).

p-*Chloro*-p'-*bromodiphenylcarbodi-imide* (XLVIII) was isolated as a yellow, viscous liquid, b. p. 198—200°/11 mm., similar in all respects to its analogues, and was identified by conversion into the carbamide.

p-*Chloro*-p'-*bromodiphenylcarbamide* (XLIX), which was also isolated from the original product, separated from much glacial acetic acid in colourless needles which melted with decomposition

at about 300° (Found: C = 48·0; H = 3·3. $C_{13}H_{10}ON_2ClBr$ requires C = 47·9; H = 3·1 per cent.).

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XIII.—*The Chlorohydrins of β-Pinene.*

By GEORGE GERALD HENDERSON and CARL ALOYSIUS KERR.

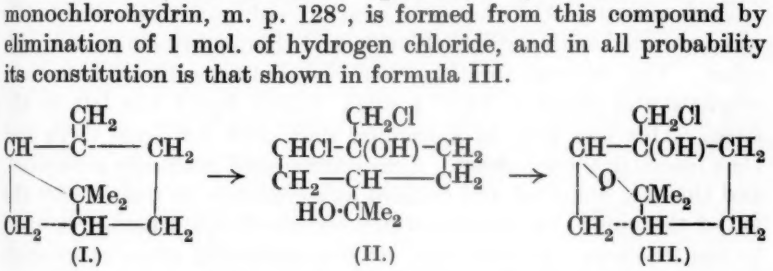
THE work described in the present paper was undertaken with the object of ascertaining if β-pinene yields dichlorohydrins on treatment with hypochlorous acid, and, in the event of such compounds being formed, of comparing their properties with those of the dichlorohydrins previously prepared from α-pinene. It has been shown (Henderson and Marsh, T., 1921, **119**, 1492) that when agitated with dilute aqueous hypochlorous acid α-pinene yields a mixture of three crystalline dichlorohydrins, $C_{10}H_{18}O_2Cl_2$, which melt at 139°, 124°, and 155° respectively, together with some tricyclene dichloride, $C_{10}H_{16}Cl_2$. These dichlorohydrins are, in fact, dichloromenthanediols, the tetramethylene ring in pinene undergoing fission under the action of the reagent, as is so often the case with that hydrocarbon. The dichlorohydrin of m. p. 139° (1 : 2-dichloromenthane-6 : 8-diol) on treatment with a dilute aqueous solution of potassium hydroxide (1 mol.), is converted into a monochlorohydrin, $C_{10}H_{17}O_2Cl$, m. p. 70°, which is easily transformed into the isomeric *i*-pinol glycol chlorohydrin, m. p. 104°, some pinol oxide being produced at the same time. On the other hand, the dichlorohydrin of m. p. 124° is directly converted by the action of dilute aqueous alkalis into the optically active form of pinol glycol chlorohydrin, m. p. 131°, together with a little of the inactive form and a trace of pinol oxide.

On treating β-pinene with a very dilute aqueous solution of hypochlorous acid we obtained a product which passed into solution and a much smaller quantity of a substance insoluble in water. The soluble product proved to be a mixture of three crystalline *dichlorohydrins*, $C_{10}H_{18}O_2Cl_2$, which melt at 135°, 166°, and 131°, respectively, together with a little of a viscous, oily substance. These dichlorohydrins are not identical, but isomeric with the corresponding compounds prepared from α-pinene.

The dichlorohydrin of m. p. 135° reacts readily with potassium hydroxide (1 mol.) in dilute aqueous solution, and yields a mono-

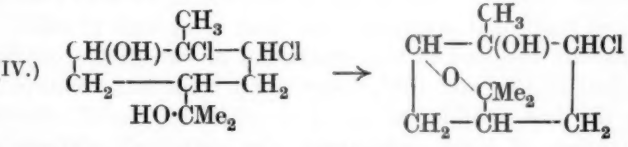
chlorohydrin, $C_{10}H_{17}O_2Cl$, which melts at 128—129°, and which, although their melting points lie close together, is not pinol glycol chlorohydrin. On treatment with a further quantity of caustic alkali the monochlorohydrin is converted into an oily liquid, which apparently is not pinol oxide although somewhat similar to it in properties. The dichlorohydrin of m. p. 166° also reacts with potassium hydroxide, but we failed to isolate any crystalline monochlorohydrin from the oily product. The product is not hydrated by the action of dilute sulphuric acid, and therefore is not pinol oxide. The third dichlorohydrin, m. p. 131°, is not attacked by dilute caustic alkalis in the cold.

The fact that β-pinene (I) combines additively with two molecular proportions of hypochlorous acid proves that fission of the tetramethylene ring occurs, and that the dichlorohydrins of β-pinene are also dichloromenthanediols. As the dichlorohydrin of m. p. 135° does not form a nitrobenzoate under the usual conditions, it probably contains only tertiary alcohol groups, and, if that is the case, must have the constitution represented by formula II. The monochlorohydrin, m. p. 128°, is formed from this compound by elimination of 1 mol. of hydrogen chloride, and in all probability its constitution is that shown in formula III.



(I.) (II.) (III.)

This appears all the more likely when it is remembered that pinol glycol chlorohydrin (V) is produced in a similar manner from sobrerol dichloride (IV).



(IV.) (V.)

Further study of the other dichlorohydrins must be undertaken before it can be decided which of the three remaining possible formulæ should be assigned to them.

Experimental.

Preparation of the Dichlorohydrins.—The β-pinene used for this work was obtained partly from French and partly from American oil of turpentine. The commercial oil was left for some time in

contact with solid potassium hydroxide and then distilled in a current of steam. As a partial separation of the constituents of the oil is effected by this process, the last third of the distillate was collected for further treatment. This portion was exhaustively fractionated with the aid of a "pear" still-head, until finally a small quantity of a liquid, which boiled constantly at 163—165°/760 mm., was obtained. This specimen of β-pinene had $d^{15°}$ 0·8710, $n_D^{15°}$ 1·4774.

β-Pinene (120 c.c.) was shaken with a 1 per cent. solution of hypochlorous acid, prepared by Taylor's method (T., 1912, **101**, 44), until the acid was completely absorbed. The reaction proceeded rapidly at first, and as soon as the odour of the acid was no longer perceptible the mixture was left to stand for a time, the aqueous layer syphoned off, and the remaining β-pinene shaken up with a fresh quantity of the solution of the acid. After several repetitions of the process a stage was reached when no more hypochlorous acid was absorbed. A layer of an oily liquid which remained undissolved was collected and examined separately.

Each quantity of the aqueous solution withdrawn from the bottle was saturated with sodium chloride and thoroughly extracted with ether. The ethereal solutions were dried over anhydrous sodium sulphate and distilled, when a thick, yellow liquid was left in the flask. This was kept in a vacuum desiccator for some days and then placed in the ice-chest. A crystalline solid gradually separated, and this was collected and drained as completely as possible by the aid of the pump, the portion which remained liquid being returned to the ice-chest. In this way, several additional crops of crystals were collected, but a part of the product remained in the form of a thick oil.

Determinations of the melting point of the partly purified crystalline substance indicated that it was a mixture of at least two compounds, and fractional crystallisation from a mixture of ether and light petroleum resulted in the separation of two dichlorohydrins, which melted at 135° and 166°, respectively: the latter compound, which is the less soluble, occurred in relatively small quantity. The separation of these substances was extremely tedious and troublesome.

The *dichlorohydrin* of m. p. 135° is a colourless solid, readily soluble in ether, methyl or ethyl alcohol, acetone, or chloroform, but sparingly soluble in light petroleum. From a mixture of ether and light petroleum it crystallises in stellate groups of fine needles. It is optically active, $[\alpha]_D^{15°}$ — 75° in methyl-alcoholic solution. When treated with *p*-nitrobenzoyl chloride in pyridine solution, it does not yield a nitrobenzoate, but it is readily converted into a

monochlorohydrin by the action of dilute aqueous potassium hydroxide in the cold (Found : Cl = 29·1. $C_{10}H_{18}O_2Cl_2$ requires Cl = 29·5 per cent.).

The *dichlorohydrin* of m. p. 166° is not quite so readily soluble in ether, alcohol, or acetone as the isomeride of m. p. 135°, and is very sparingly soluble in light petroleum. It crystallises in long, silky needles from a mixture of ether and light petroleum. It also is readily attacked by dilute aqueous alkalis in the cold, but apparently is not converted into a solid monochlorohydrin (Found : Cl = 29·6 per cent.).

A third *dichlorohydrin* was obtained, but in very small quantity, as follows. The oily residue from which the two dichlorohydrins described above had crystallised was supposed to contain more of these substances in an impure state, and in order to convert these into monochlorohydrins, was shaken with a 0·5 per cent. aqueous solution of potassium hydroxide. An emulsion was produced, but apparently there was little or no reaction of any kind, and therefore the alkali was neutralised with carbon dioxide and the liquid separated by means of ether. The ether was distilled off from the solution, and the oily residue distilled in a current of steam. Part of it volatilised in the steam and collected in the receiver in the form of a liquid, which, however, solidified on standing. It was purified by recrystallisation from a mixture of ether and light petroleum, from which it separated in colourless prisms which melted at 130—131°, and on analysis was found to contain the percentage of chlorine required for the formula $C_{10}H_{18}O_2Cl_2$ (Found : Cl = 29·2. Calc., Cl = 29·5 per cent.). Unlike the other two dichlorohydrins, it does not react with dilute aqueous potassium hydroxide in the cold. Only a small quantity of this compound was obtained, and the bulk of this was lost by an accident, so a more complete examination of it had to be postponed.

Preparation of the Monochlorohydrin.—A *monochlorohydrin* of β-pinene, $C_{10}H_{17}O_2Cl$, was prepared from the dichlorohydrin of m. p. 135°. Three grams (1 mol.) of the dichlorohydrin in fine powder were added to a 0·5 per cent. aqueous solution of 0·6 gram (1 mol.) of potassium hydroxide, and the mixture was stirred until the alkali was completely neutralised. Nearly all the dichlorohydrin passed into solution, a little being left unchanged. The solution was saturated with sodium chloride and extracted with ether, the ethereal extract washed with a little water and dried with anhydrous sodium sulphate, and the ether distilled off. A yellow, oily liquid remained, which showed no tendency to crystallise either on cooling or on treatment with solvents. In order to ascertain if pinol oxide was present, the liquid was shaken with

2 per cent. aqueous sulphuric acid. No pinol glycol was produced, but a small quantity of a crystalline *compound* separated, which, when purified by several crystallisations from ether, melted at 185°. This compound was found to contain chlorine, but was obtained in such small amount that further examination was impracticable. After separation of these crystals the residual mixture was extracted with ether, and on distillation of the ethereal solution there remained a viscous liquid, which solidified on standing, and proved to be a monochlorohydrin. When recrystallised from ether, it was obtained in colourless prisms, m. p. 128—129° (Found : Cl = 17·8. $C_{10}H_{17}O_2Cl$ requires Cl = 17·3 per cent.). The melting point of this compound is very near that of pinol glycol chlorohydrin (m. p. 131°), but the compounds are not identical, for a mixture of the two melts at 110°. When treated, in a similar manner to that just described, with potassium hydroxide (1 mol.), the monochlorohydrin is converted into an oily liquid which apparently is not pinol oxide, but was not identified on account of lack of material.

The dichlorohydrin of m. p. 166° also passes into solution when shaken with dilute aqueous potassium hydroxide (1 mol.), and from the ethereal extract of this solution, in which the alkali was completely neutralised, an oily liquid was obtained. This liquid presumably contains a monochlorohydrin, but we did not succeed in isolating such a compound in solid form, and treatment of the liquid with dilute sulphuric acid also led to no definite result, other than to prove the absence of pinol oxide.

The oily product of the action of hypochlorous acid on β-pinene which remained undissolved by the water of the solution was collected, dried, and distilled under diminished pressure. Much decomposition, with evolution of hydrogen chloride, took place as the temperature was raised, and no definite substance was isolated from the distillate except some unchanged β-pinene.

We desire to express our thanks to the Department of Scientific and Industrial Research for a maintenance grant awarded to one of us (C. A. K.), and to the Carnegie Trust for a grant in aid of the expense.

UNIVERSITY OF GLASGOW. [*Received, November 15th*, 1923.]

XIV.—*Some Oxidation Products of β-Pinene.*

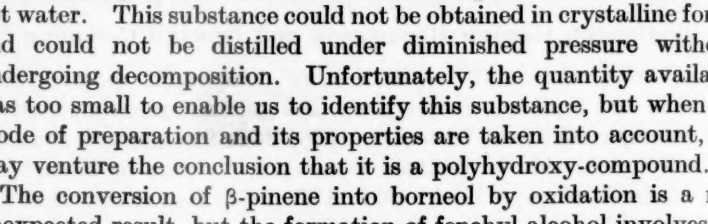
By George Gerald Henderson and Donald Chisholm.

It is known that additive and other compounds derived from α-pinene and β-pinene, respectively, are not infrequently identical. For example, Wallach (*Annalen*, 1908, **363**, 9) observed that the same hydrochloride is obtained from each of those hydrocarbons, and Pariselle (*Compt. rend.*, 1921, **172**, 1496) has shown that the addition of hydrogen bromide to each gives rise to the same product. We considered it desirable to ascertain if β-pinene also yields an additive compound on treatment with chromyl chloride, and if the oxidation products to be obtained by decomposition of the additive compound with water are identical with those formed from α-pinene in a similar manner. The latter include a saturated aldehyde, $C_{10}H_{16}O$, an unsaturated ketone, $C_9H_{14}O$, a small quantity of a crystalline compound, $C_{10}H_{15}OCl$, and a still smaller quantity of an unsaturated liquid compound, not yet identified (Henderson and Gray, T., 1903, **83**, 1299; Henderson and Heilbron, T., 1908, **93**, 288). The present investigation showed that β-pinene, like the α-isomeride, unites with chromyl chloride to form a greyish-brown solid compound of the formula $C_{10}H_{16},2CrO_2Cl_2$, which is readily decomposed by water. The chief constituent of the resulting mixture of oxidation products of β-pinene was found to be the ketone, $C_9H_{14}O$, which had been previously prepared from α-pinene, but the other products were different from those yielded by the latter hydrocarbon. An aldehyde, or probably a mixture of aldehydes, was separated, but in too small amount to permit of identification, and we also isolated a small quantity of the inactive form of *trans*-pinol glycol described by Wagner and Slawinski (*Ber.*, 1899, **32**, 2072). No trace of any chlorinated compound corresponding to the substance $C_{10}H_{15}OCl$ could be detected.

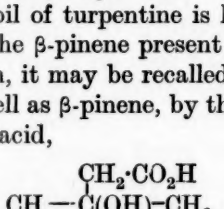
We have also, for purposes of comparison with α-pinene, examined the behaviour of β-pinene, in glacial acetic acid solution, towards hydrogen peroxide. When α-pinene is oxidised with this reagent the chief product is α-terpineol; in addition, borneol, a small quantity of dipentene, a trace of an aldehyde, and a little menthane-1 : 4 : 8-triol (trihydroxyterpan), $C_{10}H_{17}(OH)_3$, are also formed (Henderson and Sutherland, T., 1912, **101**, 2288). The products obtained by treatment of β-pinene with hydrogen peroxide were found to be for the most part quite different from these. The oily mixture of oxidation products was separated by steam distillation into a volatile and a non-volatile portion. The former was found to consist of a mixture of borneol with a little fenchyl alcohol, which

occurred chiefly as acetates. The non-volatile portion, after purification, yielded a colourless, viscous liquid which is soluble in hot water. This substance could not be obtained in crystalline form, and could not be distilled under diminished pressure without undergoing decomposition. Unfortunately, the quantity available was too small to enable us to identify this substance, but when its mode of preparation and its properties are taken into account, we may venture the conclusion that it is a polyhydroxy-compound.

The conversion of β-pinene into borneol by oxidation is a not unexpected result, but the formation of fenchyl alcohol involves an intramolecular rearrangement of a rather unusual type.



In this connexion, it is interesting to note that Bouchardat and Lafont (*Compt. rend.*, 1898, **126**, 756) obtained that alcohol, along with other products, by the action of mineral acids on oil of turpentine. Moreover, Barbier and Grignard (*Bull. Soc. chim.*, 1909, [iv], **5**, 512, 519) state that fenchyl alcohol results, along with other alcohols, when French oil of turpentine is hydrated; they assume that it is formed from the β-pinene present in this variety of oil of turpentine. In addition, it may be recalled that Wallach (*loc. cit.*) obtained fenchene, as well as β-pinene, by the action of dehydrating agents on nopinolacetic acid,



EXPERIMENTAL.

Separation of β-Pinene.—The β-pinene used in our experiments was prepared by fractional distillation of both French and American oil of turpentine. From consideration of Pariselle's results (*Ann. chim.*, 1923, [ix], **19**, 119) it appeared probable that the French oil would give the better yield, but our experience was similar to that of Wallach (*loc. cit.*), for we found the American oil to be slightly richer in β-pinene than the French variety. The oil of turpentine, after standing in contact with solid potassium hydroxide for some days, was distilled in a current of steam, and the last third of the dis-

tillate was collected, dried, and fractionated with the aid of a " pear " still-head. The portion which passed over at 155—156° consisted almost wholly of α-pinene and was set aside. Fractions of the remaining oil were taken, at intervals of 1°, up to 166°, and those which distilled between 160° and 166° were further fractionated by means of a " modified evaporator " still-head with three compartments. Ultimately, after exhaustive fractionation, a portion which boiled constantly at 163—165° was isolated. This specimen of β-pinene had $d^{18°}$ 0·8710, $n_D^{18°}$ 1·4770.

The yield of this fraction was little more than 1 per cent. of the oil of turpentine taken.

Oxidation of β-Pinene with Chromyl Chloride.—A greyish-brown solid compound of the formula $C_{10}H_{16},2CrO_2Cl_2$ was obtained by the slow addition of a 10 per cent. solution of 100 grams of chromyl chloride in carbon disulphide to a solution of 40 grams of β-pinene in 400 grams of the same solvent, which was well cooled and constantly agitated during the process. After a small excess of the reagent had been added the precipitate was left to settle, the supernatant liquid decanted, and the pasty mixture of the additive compound with carbon disulphide which remained poured slowly into ice-cold water, which was vigorously agitated. The mixture was finally warmed gently in order to complete the decomposition of the compound, the carbon disulphide layer (which contained the bulk of the oxidation products) separated, and the aqueous layer extracted several times with ether and finally with light petroleum. The several solutions were washed with water and dried over anhydrous sodium sulphate, and, on removal of the solvents by distillation, the crude oxidation product was left in the form of a thick brown oil. This was distilled in a current of steam, when an oily liquid passed over into the receiver whilst a considerable proportion of resinous matter was left in the distilling flask. The distillate was extracted with ether and the ethereal solution dried and distilled.

The liquid thus obtained was mixed with an equal volume of a freshly prepared saturated solution of sodium bisulphite and kept in a cool place, with occasional agitation, for several weeks, when a small crop of crystals of a bisulphite compound was slowly deposited. The crystals were collected, washed successively with alcohol and with ether, and dried. The liquid was extracted from the filtrate with ether and again treated with sodium bisulphite solution, with the result that a second but very small crop of crystals was obtained. The bisulphite compound was then distilled with an aqueous solution of sodium carbonate and the liberated aldehyde, which collected in a semi-solid state in the receiver, was taken up in ether. After removal of the ether by distillation there remained a very small

quantity of a thick, greenish-yellow oil, which had a strong characteristic odour. This was converted into a semicarbazone by treatment with semicarbazide hydrochloride and potassium acetate, and the solid product was recrystallised from methyl alcohol. It separated from this solvent in white nodules, which when heated began to soften at 30° and liquefied completely at 50°. The crystalline product therefore appeared to consist of a mixture of two semicarbazones, but attempts to separate these by fractional crystallisation were not successful, on account of the very small quantity at our disposal. The semicarbazone of the aldehyde similarly obtained from α-pinene melts at 191°.

The ethereal solution of the liquid which remained after this treatment with sodium bisulphite was washed with aqueous sodium carbonate and with water, dried over anhydrous sodium sulphate, and distilled. The residual liquid, dissolved in methyl alcohol, was treated with the requisite quantities of semicarbazide hydrochloride and potassium acetate, and after some time crystals of a semicarbazone were deposited. Water was then added gradually to the solution until no further separation of crystals took place. After purification by recrystallisation from methyl alcohol, the semicarbazone was found to melt, with decomposition, at 225°. The semicarbazone of the ketone $C_9H_{14}O$, prepared in a similar manner from α-pinene by Henderson and Gray (*loc. cit.*), melts at 226°, and a mixture of the two melts at the same temperature. The identity of the two semicarbazones was thus proved. The ketone itself was obtained by boiling its semicarbazone with a slight excess of aqueous oxalic acid and extracting the distillate with ether. It is a colourless liquid with a pleasant odour, which boils at 207—208°/760 mm., decolorises potassium permanganate, unites with two atomic proportions of bromine, and in short has the same properties as the ketone obtained from α-pinene.

The aqueous-alcoholic solution from which the ketone semicarbazone had separated was observed to possess a peculiar penetrating odour and to become turbid on addition of a larger quantity of water. It was therefore diluted with water and distilled, and the turbid distillate was extracted several times with ether. The ethereal solution was washed with small quantities of water and dried, and the ether was removed by evaporation under diminished pressure. A small quantity of a white, crystalline solid remained, which, after recrystallisation from ether, melted at 125°. The compound has a strong odour, sublimes readily, volatilises very easily in a current of steam or of alcohol vapour, and gives a golden-yellow coloration with concentrated sulphuric acid (Found : C = 64·4; H = 9·9. $C_{10}H_{18}O_3$ requires C = 64·5; H = 9·7 per cent.).

Thus it appears that the compound is the inactive form of *trans*-pinol glycol.

Oxidation of β-Pinene with Hydrogen Peroxide.—The oxidation was effected as follows. Eighty c.c. of 30 per cent. aqueous hydrogen peroxide (2 mols.) were added to a solution of 50 grams of β-pinene (1 mol.) in 130 grams of glacial acetic acid, and the mixture was heated, under reflux, in a water-bath at 50—55° until the β-pinene, which separated on addition of the solution of hydrogen peroxide, had again passed completely into solution. Under these conditions the reaction proceeded slowly, but attempts to hasten it by raising the temperature resulted in the formation of much resinous matter. After constant heating for eight days the oxidation of the β-pinene appeared to be completed, and the acetic acid in the liquid was then neutralised with sodium carbonate, water being added in sufficient quantity to keep the salt in solution. The oily product which separated was extracted with ether, and the aqueous layer shaken up repeatedly with ether until a test showed that nothing more was extracted.

In order to ascertain if any acid formed by oxidation of the β-pinene was present in the aqueous solution, it was acidified with dilute sulphuric acid and extracted with ether. No acid other than acetic acid was found in the ethereal extract.

The ethereal solution of the oxidation products was washed with water and dried, and on removal of the ether by distillation a viscous, brown liquid was obtained. Portions of this were tested for aldehydes or ketones with aqueous sodium bisulphite and with semicarbazide acetate, but the results were negative. The liquid was then distilled in a current of steam, when about three-fourths passed over, the non-volatile part remaining in the distilling flask as a brown, resinous mass. The volatile portion was extracted from the distillate with ether, and on removal of the solvent was left in the form of a colourless liquid with a pleasant odour. It was now heated for fifteen minutes, under reflux, with a methyl-alcoholic solution of the requisite quantity of potassium hydroxide, and then the alkali was neutralised with carbon dioxide, the alcohol distilled off, and the residual liquid heated in a current of steam. On acidification of the solution remaining in the distilling flask, acetic acid was liberated, but no other acid could be detected. The distillate was extracted with ether, the ethereal solution dried, the ether removed, and the oily liquid which remained was distilled under diminished pressure. Practically the whole passed over between 116° and 120° at 20 mm., with no sign of separation into fractions. A portion of the distillate was examined to ascertain if it contained α-terpineol, but we failed to detect any of that com-

pound. On proceeding to prepare a nitrobenzoate from another portion, we found that only a part of the liquid reacted readily under the conditions of the preparation, and this observation suggested a method for the separation of the constituents. The liquid was dissolved in ten times its weight of pyridine and finely powdered *p*-nitrobenzoyl chloride was slowly added, in quantity amounting to about two-thirds of that required for the complete conversion of the alcohol into a nitrobenzoate. The mixture was gently warmed on the water-bath for two days, and on cooling set to a crystalline mass. The crystals were collected with the aid of the pump, washed with dilute sulphuric acid and with water, agitated with dilute aqueous sodium carbonate, washed with water, and finally crystallised from methyl alcohol. After several crystallisations, the *p*-nitrobenzoate was obtained in glistening, colourless plates, m. p. 137°. A mixture of this compound with borneol *p*-nitrobenzoate (m. p. 137°) was found to melt at the same temperature, hence the presence of borneol among the products of oxidation was proved.

The pyridine solution from which the borneol *p*-nitrobenzoate had crystallised was mixed with a slight excess of dilute sulphuric acid and the precipitated nitrobenzoic acid drained with the aid of the pump. A small quantity of a brown, oily liquid, which was observed to float on the surface of the filtrate, was extracted by means of ether and, after removal of the ether, distilled in a current of steam. A white, waxy solid separated from the water in the receiver, and when dried was found to melt at 40°. It had an unpleasant odour resembling that of fenchyl alcohol. For comparison, some fenchyl alcohol was prepared by reducing *d*-fenchone in alcoholic solution with sodium. The specimen so obtained melted at 42°, and no lowering of the melting point was observed when our product was mixed with this. It therefore appears that fenchyl alcohol also is produced by the oxidation of β-pinene with hydrogen peroxide.

The portion of the mixture of oxidation products which did not volatilise in steam was heated under reflux with methyl-alcoholic potassium hydroxide for a short time. After neutralising the alkali with carbon dioxide, the alcohol was distilled off and the aqueous solution thoroughly extracted with ether. The aqueous solution was then acidified and extracted with ether, but acetic acid was the only acid detected. The ethereal solution of the neutral substance was washed with a little water and dried, and when the ether was distilled off, a small quantity of a dark brown, viscous liquid was obtained. This was found to dissolve in boiling water. The solution was decolorised by means of animal charcoal and then saturated with ammonium sulphate and repeatedly extracted with ether.

The ethereal solution was washed with a little water, dried, and distilled, with the result that a colourless, very viscous liquid was left in the flask. All attempts to obtain this substance in crystalline form, by cooling and by treatment with a number of different solvents, were unsuccessful, and when a portion was heated under diminished pressure practically complete decomposition took place. The quantity of the substance available was so small that we were unable to identify it, but in all probability it is a polyhydric alcohol.

We take this opportunity of expressing our indebtedness to the Department of Scientific and Industrial Research for awarding a maintenance grant to one of us (D. C.), and to the Carnegie Trust, for a grant which helped to defray the expense of the work.

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XV.—*Preparation of 2 : 4 : 2′ : 4′-Tetrahydroxybenzophenone.*

By JOHN BALDWIN SHOESMITH and JOHN HALDANE.

2 : 4 : 2′ : 4′-TETRAHYDROXYBENZOPHENONE was first prepared by Meyer and Conzetti (*Ber.*, 1897, **30**, 971), who fused fluorescein chloride with caustic soda at 270—280°. The present investigation has shown that the method used first by Hoesch (*Ber.*, 1915, **48**, 1122) to prepare aromatic hydroxyketones is also applicable to the synthesis of this ketone.

2 : 4-Diacetoxybenzonitrile, $C_6H_3(OAc)_2{\cdot}CN$, and resorcinol condense in presence of hydrochloric acid. 2 : 4-Diacetoxy-2′ : 4′-dihydroxybenzophenoneimine hydrochloride,

$$(OAc)_2C_6H_3{\cdot}C(:NH,HCl){\cdot}C_6H_3(OH)_2,$$

thus formed, is moderately easily hydrolysed in acid solution to the expected benzophenone. From the reaction product, resacetophenone, $C_6H_3(OH)_2{\cdot}CO{\cdot}CH_3$, and β-resorcylamide may also be isolated. The former is produced by the condensation of acetyl chloride (from diacetoxybenzonitrile and hydrochloric acid) with resorcinol, and the latter by the hydrolysis of unchanged diacetoxybenzonitrile.

The compound described by Marcus (*Ber.*, 1891, **24**, 3652) as β-resorcylonitrile will not condense with resorcinol.

EXPERIMENTAL.

2 : 4-Diacetoxybenzonitrile (7 grams), prepared as described by Marcus (*loc. cit.*), and carefully dried resorcinol (2·5 grams) were

dissolved in 40 c.c. of dry ether, powdered anhydrous zinc chloride (1 gram) was added, and a slow stream of hydrogen chloride gas passed into the reaction mixture. Turbidity was apparent after four hours, and a crystalline precipitate formed almost immediately afterwards. The hydrogen chloride gas was passed for eight hours and after that the mixture allowed to stand for another twelve hours. The ether was then poured off from the crystals and from it, after standing some days, an additional quantity of the crystals separated out. The crystals were dissolved in cold water and precipitated with concentrated hydrochloric acid. The solid was purified by the repetition of this process at least twice, and after having been dried decomposed at 195° and proved to be 2 : 4-*diacetoxy*-2′ : 4′-*dihydroxybenzophenoneimine hydrochloride* (Found : Cl = 9·7. $C_{17}H_{16}O_6NCl$ requires Cl = 9·5 per cent.). The hydrochloride was hydrolysed by boiling 25 per cent. aqueous sulphuric acid, the operation being complete in about fifteen minutes. The cooled solution deposited a syrup which was then boiled with dilute sodium carbonate solution for half an hour. From this solution yellow crystals separated (2 grams) which were recrystallised from boiling water and animal charcoal and possessed all the properties of the 2 : 4 : 2′ : 4′-tetrahydroxybenzophenone obtained by the method of Meyer and Conzetti (*loc. cit.*).

β-*Resorcylamide.*—The acid solution from the hydrolysis of the imine hydrochloride was extracted with ether several times and the combined extracts were mixed with the ether from which the imine hydrochloride had separated. When the ether was distilled away from the extract, a syrup remained from which white, needle-shaped crystals were at once precipitated on the addition of water. This solid was recrystallised from water, when it melted at 221—222°. Its aqueous solution gave a reddish-brown coloration with ferric chloride. Ammonia was evolved (*a*) slowly from a boiling caustic soda solution of the solid, (*b*) more rapidly if the solid was first hydrolysed with 50 per cent. sulphuric acid and then boiled with caustic soda, (*c*) immediately when the solid was heated alone. The compound was classified as β-resorcylamide (Found : C = 55·14; H = 5·02; N = 9·03. Calc. for $C_7H_8O_3N$, C = 54·90; H = 4·58; N = 9·15 per cent.). After the hydrolysis of the amide a small quantity of β-resorcylic acid was isolated from the solution.

Resacetophenone.—The aqueous solution from which the β-resorcylamide had been precipitated was extracted with ether and the syrup remaining after the ether had been distilled off boiled with dilute hydrochloric acid and animal charcoal. From this solution, white needles crystallised out which when purified melted at 141—142° and easily gave a phenylhydrazone with melting point 158°.

This ketone did not depress the melting point of an authentic specimen of resacetophenone.

Attempts were made to prepare β-resorcylonitrile. 2 : 4-Diacetoxybenzonitrile was boiled with caustic alkali (or dilute sulphuric acid) of different concentrations for varying periods of time. The hydrolysed mixtures were extracted with ether and the solid fractionally precipitated by the addition of ligroin. Analysis showed that the nitrogen content varied with the conditions of hydrolysis and pure β-resorcylonitrile could not be isolated. The white needles obtained would not condense with resorcinol under the same conditions as those used in the condensation of 2 : 4-diacetoxybenzonitrile.

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XVI.—*The Decomposition of Substituted Carbamyl Chlorides by Hydroxy-compounds. Part I. The Reaction between Phenylmethylcarbamyl Chloride and Ethyl Alcohol at Different Temperatures.*

By TUDOR WILLIAMS PRICE.

WHILST it is well known that substituted carbamyl chlorides of the type RR′N·COCl react readily with hydroxy-compounds, the kinetics of the reactions do not seem to have been studied.

The general equation for the reaction is

$$RR'N\cdot COCl + R''OH = RR'N\cdot CO_2R'' + HCl,$$

the products being hydrogen chloride and an ester of a substituted carbamic acid. When the hydroxy-compound employed is water, a substituted carbamic acid, $RR'N\cdot CO_2H$, is formed, which loses carbon dioxide to give a secondary amine, NHRR′.

The ease with which chlorine is removed from the carbamyl chloride would presumably depend on the constitution of the carbamyl chloride and of the hydroxy-compound. It therefore seemed of interest to undertake a systematic investigation into the kinetics of the reaction. Of especial interest would be the comparison between the effects of alcohols and water, obtained by a determination of the rate of the reaction of a given carbamyl chloride with an alcohol, with water, and with mixtures of the two. In the

last case—owing to the different nature of the products of reaction, since water gives carbon dioxide as well as hydrogen chloride, whilst an alcohol does not—it ought to be possible to determine how much of the carbamyl chloride reacts with the water and how much with the alcohol.

In the present communication an account is given of the rate of reaction between phenylmethylcarbamyl chloride and ethyl alcohol at various temperatures.

Experimental.

Preparation of Materials.—Phenylmethylcarbamyl chloride was prepared by the interaction of carbonyl chloride and pure methylaniline in toluene. The product, after removal of unchanged methylaniline, hydrogen chloride, and toluene, was distilled under reduced pressure (15—18 mm.). A slightly yellow solid, smelling faintly of carbimide, was obtained. This was purified by dissolving in cold glacial acetic acid and pouring into water. The product was well washed, thoroughly dried, and recrystallised twice from boiling light petroleum (b. p. 80—100°). The product, m. p. 87·5° (uncorr.) was snow-white and remained so as long as it was kept in a desiccator over phosphorus pentoxide. Exposure to the atmosphere gradually caused it to acquire a faintly green tinge, which, however, could be removed by the above treatment with glacial acetic acid, followed by crystallisation from light petroleum.

The carbamyl chloride was analysed by heating with excess of alcoholic potassium hydroxide and titrating with $N/10$-silver nitrate (Found: Cl = 20·86. Calc., Cl = 20·94 per cent.).

The ethyl alcohol was commercial absolute alcohol which had been treated twice at the boiling point with fresh calcium turnings (1·0 and 0·5 per cent. by weight) and fractionated. It distilled sharply at 78·6° (uncorr.).

Method of Work.—Preliminary experiments showed that the reaction proceeded very slowly at all temperatures below the boiling point of ethyl alcohol; consequently it was decided to determine the rate of the reaction at higher temperatures also, namely, 100°, 90°, 80°, and 70°. This necessitated the use of sealed tubes, consequently the hydrogen chloride formed, being kept in the system, reacted with the ethyl alcohol to form ethyl chloride. Thus two consecutive reactions proceeded as follows:

(1) $NMePh{\cdot}COCl + EtOH = NMePh{\cdot}CO_2Et + HCl.$
(2) $HCl + EtOH = EtCl + H_2O.$

According to the chemical equations, these are two consecutive bimolecular reactions, but by using a large excess of ethyl alcohol,

the reaction was made unimolecular with respect to the carbamyl chloride or the hydrogen chloride.

These two reactions are both reversible, but experiments (as yet unpublished) made by the author on the hydrolysis of phenylmethylurethane by hydrogen chloride show that the velocity of the back reaction in the first case is exceedingly slow as compared with the forward reaction, and the equilibrium point corresponds with more than 95 per cent. of the carbamyl chloride being transformed.

A thorough investigation of the action of ethyl alcohol on phenylmethylcarbamyl chloride under the above conditions of experiment would include a study of (A) the reaction represented by equation (1) alone, (B) the reaction represented by equation (2) alone, (C) the two reactions together.

This was done by the methods shown below.

(A) *Investigation of the Reaction between Phenylmethylcarbamyl Chloride and Ethyl Alcohol.*

In order to investigate this reaction separately, it is necessary to prevent the hydrogen chloride which is produced from reacting with the excess ethyl alcohol. For this purpose a weak base, which would not react with the carbamyl chloride, and would allow the hydrogen chloride to be titrated completely by potassium hydroxide, was added. Pyridine was first tried, but without success, since it produced a blood-red coloration with the carbamyl chloride after a few minutes' heating at 100°. Dimethylaniline served the purpose, but it was found that the velocity of the reaction between the carbamyl chloride and ethyl alcohol depended on the quantity of dimethylaniline added. The greater the quantity of dimethylaniline added, the slower the reaction became. This difficulty was overcome by making three series of experiments at the same temperature, using different quantities of dimethylaniline, namely, 0·5 c.c., 1·0 c.c., and 1·5 c.c., respectively, for the same quantities of phenylmethylcarbamyl chloride (0·424 gram) and ethyl alcohol (5 c.c.). Tubes containing these quantities were sealed and heated for various periods. (0·5 C.c. of dimethylaniline was a little more than the theoretical quantity required to combine with all the hydrogen chloride formed.)

The velocity coefficient was calculated for each series and, by extrapolation, the velocity coefficient corresponding to the reaction without any addition of dimethylaniline was obtained.

This velocity coefficient could also be calculated from the results under section (C), where the concentration of phenylmethylcarbamyl chloride at any instant could be obtained. The two values for the velocity coefficient agreed satisfactorily and consequently experi-

ments under section (A) were carried out at one temperature only, 100°.

(B) *Investigation of the Reaction between Ethyl Alcohol and Hydrogen Chloride.*

This was carried out by heating $N/2$-alcoholic hydrogen chloride (this being the same concentration as that of the carbamyl chloride in the other sections) in sealed tubes for varying intervals of time at the necessary temperatures, and then titrating with $N/10$-potassium hydroxide, using methyl-orange as indicator. The $N/2$-alcoholic hydrogen chloride was made up by passing dry hydrogen chloride into dry alcohol (kept at 0°) and adjusting until the required concentration was obtained. Five c.c. of the $N/2$-solution were used in each experiment.

(C) *Investigation of the Two Consecutive Reactions Together.*

At any instant after the commencement of the reaction there are present phenylmethylcarbamyl chloride, ethyl alcohol (in large excess), phenylmethylurethane, hydrogen chloride, ethyl chloride, and water. Reference to the equations will show that a knowledge of the amount of phenylmethylcarbamyl chloride, hydrogen chloride, and ethyl chloride present at any time will suffice to characterise the whole reaction. If a is the initial amount of phenylmethylcarbamyl chloride, and x, y, and z are the amounts of phenylmethylcarbamyl chloride, hydrogen chloride, and ethyl chloride, respectively, present after a time t, then $a = x + y + z$.

The procedure adopted for the estimation of these three substances was as follows:

0·424 Gram of phenylmethylcarbamyl chloride was weighed into a hard glass test-tube, 5 c.c. of ethyl alcohol were added, and the tube was sealed. This, taking into consideration the purity of the substance, gave a $N/2$-solution. The tubes were placed in a thermostat, at the required temperature, for varying intervals and then quickly cooled. The contents were washed out with alcohol and then with water and quickly titrated with $N/10$-potassium hydroxide and methyl-orange. This gave the quantity of hydrogen chloride present (y). Air was then aspirated through for thirty minutes to remove the ethyl chloride. Excess of solid potassium hydroxide was added and the contents were heated under a reflux condenser for twelve hours. Pure nitric acid was added and the chloride present was titrated with $N/10$-silver nitrate without an indicator. This gave the total chloride present in the system (after removal of ethyl chloride), which is equal to $x + y$. Subtraction of the hydrogen chloride gave the phenylmethylcarbamyl chloride (x)

present. The difference between the original quantity of carbamyl chloride used (a) and the total chloride as determined above ($x + y$) gave the amount of ethyl chloride (z) which had been removed by aspiration of air.

Results.

Section A. Action of Ethyl Alcohol on Phenylmethylcarbamyl Chloride in presence of Dimethylaniline at 100°.—In this section the first column gives the duration of the experiment in minutes, the second column gives the amount of hydrogen chloride present, expressed as c.c. of N/10-solution, as determined by titration with N/10-potassium hydroxide, the third column gives the amount of phenylmethylcarbamyl chloride present, expressed as c.c. of N/10-solution, and obtained by subtracting the amount of N/10-hydrogen chloride from the initial quantity of carbamyl chloride (equal to 25 c.c. of N/10-solution), and the fourth column gives the velocity coefficient calculated for a unimolecular reaction,

$$k = \frac{1}{t_2 - t_1} \log_e \frac{a - x_1}{a - x_2}.$$

This expression for the velocity coefficient was used in all three sections, t_1 being five minutes, in order to obviate the initial disturbances due to the solution being made up at room temperature and the experiments being carried out at elevated temperatures.

Series I. 0·424 Gram of phenylmethylcarbamyl chloride + 5 c.c. of alcohol + 0·5 c.c. of dimethylaniline.

Time (mins.).	C.c. of N/10-HCl.	Carbamyl chloride present. C.c. of N/10-soln.	k.	Time (mins.).	C.c. of N/10-HCl.	Carbamyl chloride present. C.c. of N/10-soln.	k.
5	2·75	22·25	—	30	16·25	8·75	0·0373
10	6·38	18·62	0·0356	60	22·47	2·53	0·0395
15	9·34	15·66	0·0351	180	25·02	0·0	—
20	12·17	12·83	0·0367				

Mean value (omitting the last one) $k = 0·0362$.

Series II.

With 1·0 c.c. of dimethylaniline.
Limits of k 0·0299—0·0322.
Mean value of k (7 determinations) = 0·0307.
Limits of time 5—210 minutes.

Series III.

With 1·5 c.c. of dimethylaniline.
Limits of k 0·0248—0·0272.
Mean value of k (7 determinations) = 0·0261.
Limits of time 5—65 minutes.

Extrapolation, using Lagrange's formula, gives $k = 0·0426$ for the reaction when no dimethylaniline is present.

Section B. Action of Hydrogen Chloride on Ethyl Alcohol.—The first column gives the duration of the experiment in minutes, the second column gives the amount of hydrogen chloride present, expressed as c.c. of $N/10$-solution, and the third column gives the velocity coefficient, calculated for a unimolecular reaction.

Series IV. Temp. 100°. $N/2$-Alcoholic HCl, factor = 1·002.

Time (mins.).	C.c. of $N/10$-HCl.	k.	Time (mins.).	C.c. of $N/10$-HCl.	k.
5	23·80	—	95	10·43	0·0092
20	20·33	0·0105	125	8·23	0·0088
35	17·56	0·0101	245	3·99	0·0074
50	15·17	0·0100	365	2·45	0·0063
65	13·32	0·0097	485	1·55	0·0057

k (mean of first three values) = 0·0102.

Series V. Temp. 90°. $N/2$-Alcoholic HCl, factor = 1·002.

Results similar to those in series IV. k (mean of first three values) = 0·00443.

Series VI. Temp. 80°. $N/2$-Alcoholic HCl, factor = 1·000.

Results similar to those in series IV. k (mean of first three values) = 0·00162.

Series VII. Temp. 70°. $N/2$-Alcoholic HCl, factor = 0·990.

Results similar to those in series IV. k (mean of first three values) = 0·000521.

The velocity coefficient, calculated for a unimolecular reaction, falls steadily in each series, since the reaction is reversible and no account has been taken of the back reaction.

Section C.—In this section are given the results of an investigation of the two consecutive reactions proceeding in the same tube. The concentrations throughout are expressed as c.c. of $N/10$-solution. The first column gives the duration of the experiment in minutes, the second gives the amount of hydrogen chloride present, as determined by titration with $N/10$-potassium hydroxide, and the third gives the amount of hydrogen chloride plus phenylmethylcarbamyl chloride present, as determined by titration with $N/10$-silver nitrate after removal of ethyl chloride; this is called the total chloride; the fourth column gives the amount of phenylmethylcarbamyl chloride present, and is obtained by subtracting the figures in column 2 from those in column 3; the fifth column gives the amount of ethyl chloride present, obtained by subtracting the total chloride

in column 3 from the initial amount of carbamyl chloride used, which was equivalent to 25 c.c. of $N/10$-solution. The sixth column gives the velocity coefficient, for the reaction between phenylmethylcarbamyl chloride and ethyl alcohol, calculated for a unimolecular reaction from the figures in column 4. In each experiment 0·424 gram of phenylmethylcarbamyl chloride and 5 c.c. of ethyl alcohol were used.

Time (mins.).	C.c. of $N/10$-HCl.	Total chloride. C.c. of $N/10$-soln.	Carbamyl chloride. C.c. of $N/10$-soln.	Ethyl chloride. C.c. of $N/10$-soln.	k.
		Series VIII. Temp. 100°.			
5	2·54	24·47	21·93	0·53	—
10	6·39	24·13	17·74	0·87	0·0424
15	9·46	23·89	14·43	1·11	0·0419
20	11·50	23·24	11·74	1·76	0·0417
30	14·44	22·00	7·56	3·00	0·0426
35	15·02	20·95	5·93	4·05	0·0436
40	15·55	20·42	4·87	4·58	0·0430
45	15·57	19·38	3·81	5·62	0·0437
50	15·38	18·60	3·22	6·40	0·0426
65	14·78	16·48	1·70	8·52	0·0426
80	13·40	14·35	0·95	10·65	
95	12·10	13·01	0·91	11·99	
125	10·27	11·07	0·80	13·93	
245	4·27	4·76	0·49	20·24	
365	2·41	2·87	0·46	22·13	
485	1·17	1·67	0·50	23·33	
725	0·57	1·10	0·53	23·90	Mean
1085	0·25	0·79	0·54	24·21	0·0427
		Series IX. Temp. 90°.			
5	1·37	24·98	23·61	0·02	—
10	3·50	24·90	21·40	0·10	0·0197
15	5·30	24·75	19·45	0·25	0·0194
20	6·82	24·50	17·68	0·50	0·0193
30	9·57	24·01	14·44	0·99	0·0197
40	11·71	23·71	12·00	1·29	0·0193
50	13·40	23·10	9·70	1·90	0·0198
65	14·87	22·08	7·21	2·92	0·0198
80	15·27	20·70	5·43	4·20	0·0196
95	15·71	19·72	4·01	5·28	0·0197
110	15·91	18·85	2·94	6·15	0·0198
125	15·71	17·88	2·17	7·12	0·0199
155	13·96	15·17	1·21	9·83	0·0186
185	12·86	13·75	0·89	11·25	0·0169
215	11·68	12·34	0·66	12·66	
245	10·72	11·28	0·56	13·72	
365	7·83	8·41	0·58	16·59	
545	4·53	5·14	0·56	19·86	Mean
785	2·92	3·43	0·51	21·57	0·0196 *

* The last two values, where the reaction has almost come to equilibrium, are excluded.

Time (mins.).	C.c. of $N/10$-HCl.	Total chloride. C.c. of $N/10$-soln.	Carbamyl chloride. C.c. of $N/10$-soln.	Ethyl chloride. C.c. of $N/10$-soln.	k.
		Series X.	Temp. 80°.		
5	0·47	24·97	24·50	0·03	—
15	2·24	24·74	22·50	0·26	0·00852
35	5·55	24·50	18·95	0·50	0·00856
60	9·00	24·25	15·25	0·75	0·00862
85	11·67	23·76	12·09	1·24	0·00909
110	13·45	23·42	9·97	1·58	0·00856
135	15·03	22·85	7·82	2·15	0·00879
160	15·95	22·25	6·30	2·75	0·00876
180	16·36	21·62	5·26	3·38	0·00879
200	16·66	21·03	4·37	3·97	0·00884
220	16·83	20·58	3·75	4·42	0·00873
240	16·95	20·03	3·08	4·97	0·00882
260	16·93	19·53	2·60	5·47	0·00879
280	16·90	19·17	2·27	5·83	0·00865
320	16·66	18·07	1·41	6·93	
380	15·77	16·70	0·93	8·30	
500	13·87	14·39	0·52	10·61	
740	10·75	11·24	0·49	13·76	
1100	7·48	7·95	0·47	17·05	Mean
1800	4·45	4·86	0·41	20·14	0·00873
		Series XI.	Temp. 70°.		
5	0·18	25·00	24·82	0·00	—
65	4·07	24·44	20·37	0·56	0·00329
125	7·49	24·31	16·82	0·69	0·00324
185	10·29	24·06	13·77	0·94	0·00327
245	12·23	23·62	11·39	1·38	0·00325
305	14·19	23·44	9·25	1·56	0·00329
365	15·46	22·93	7·47	2·07	0·00334
425	16·28	22·32	6·04	2·68	0·00336
485	16·90	22·08	5·18	2·92	0·00325
545	17·17	21·27	4·10	3·73	0·00335
605	17·38	20·91	3·53	4·09	0·00325
665	17·53	20·30	2·77	4·70	0·00331
725	17·51	19·76	2·26	5·24	0·00333
785	17·50	19·18	1·58	5·82	
1000	16·59	17·39	0·80	7·61	
1500	13·70	14·23	0·53	10·77	
2355	10·22	10·78	0·56	14·22	
3400	7·40	7·97	0·57	17·03	
4550	5·70	6·25	0·55	18·75	Mean
5550	4·60	5·14	0·54	19·86	0·00329

Discussion of the Results.

The results in section A show that the velocity of the reaction between phenylmethylcarbamyl chloride and ethyl alcohol, under such conditions that the hydrogen chloride formed is prevented from reacting with the alcohol owing to the presence of dimethylaniline, is dependent on the amount of dimethylaniline present. The *rôle* played by the dimethylaniline is at present obscure. It does not react with the carbamyl chloride in such a way as to split off hydrogen chloride, since on heating 0·424 gram of phenylmethylcarbamyl

chloride with 1·5 c.c. of dimethylaniline and 5 c.c. of light petroleum —which contains no hydroxyl group—for thirty minutes at 100°, no acidity was developed. Again it does not react with the carbamyl chloride in such a way as to prevent any of the chlorine originally present from being converted into hydrogen chloride by the action of ethyl alcohol, since the results show that the whole of the chlorine of the carbamyl chloride is converted into hydrogen chloride by alcohol even in the presence of dimethylaniline. The only effect of the dimethylaniline seems to be to retard the action, but not to prevent it going to completion. Further work is necessary to elucidate this action.

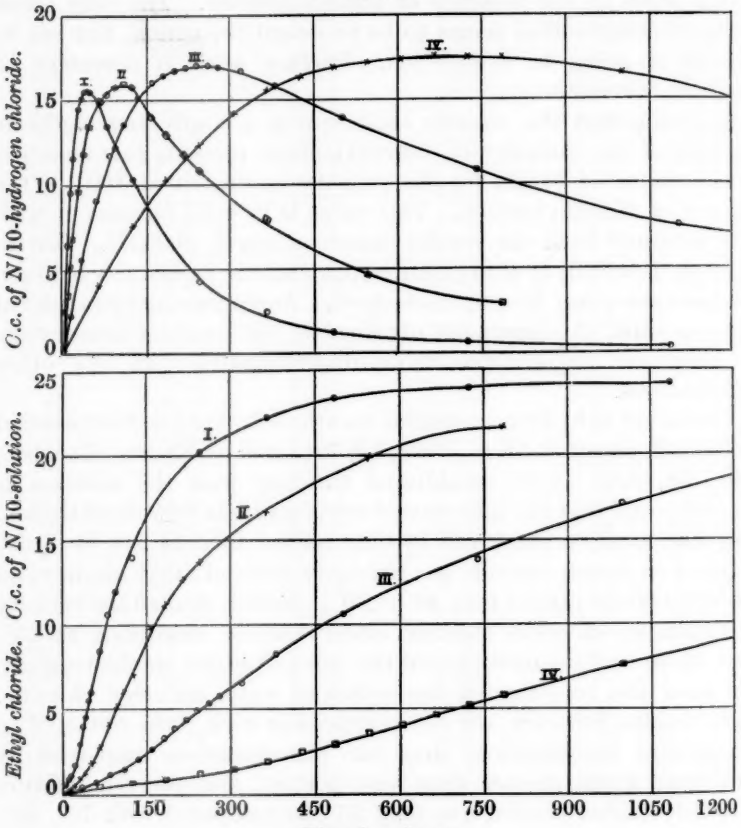
Assuming that the velocity coefficient is a continuous algebraic function of the quantity of dimethylaniline present, extrapolation gives a value of 0·0426 for the velocity coefficient at 100° in the absence of dimethylaniline. This value is in good agreement with that obtained from the results under section C (0·0427). Extrapolation, however, is always dangerous and the agreement between the two values may be quite fortuitous. Accepting the extrapolated value as valid, the agreement obtained at 100° made it unnecessary to carry out experiments using dimethylaniline at the other temperatures.

The action of hydrogen chloride on ethyl alcohol has been studied by Cain (*Z. physikal. Chem.*, 1893, **12**, 751), and by Kailan (*Monatsh.*, 1907, **28**, 559). Cain established the fact that the reaction is reversible and that the influence of temperature is very considerable. The concentration employed by Cain ranged from 31·2 to 81 equivalents of hydrogen chloride per 100 equivalents of ethyl alcohol and the temperature ranged from 40° to 99°. Kailan studied the velocity of formation of ethyl chloride under various conditions at 25°. Both these workers investigated the effect of water on the reaction, and Cain also investigated the action of water on ethyl chloride. Their results, however, are not comparable with those obtained in the present investigation, since the concentrations employed by Cain were much greater than semi-normal, and the temperature at which Kailan worked was only 25°, as compared with 70°, 80°, 90°, and 100° in section B of this communication.

The results obtained in section C are typical of those for two consecutive reactions. This is brought out most clearly in the accompanying diagrams. Fig. 1 shows how the amount of hydrogen chloride present varies with time at 100°, 90°, 80°, and 70°. At each temperature the hydrogen chloride content rises to a maximum, and then falls until equilibrium is attained. The effect of temperature on the reaction is shown by the varying time taken for the maximum point to be reached at the different temperatures; the

higher the temperature, the more quickly is the maximum reached. Again, the absolute amount of hydrogen chloride present at the maximum point increases as the temperature becomes lower. This shows that the second reaction, by which hydrogen chloride is consumed, slows down more quickly with decreasing temperature than does the first reaction, by which hydrogen chloride is generated.

FIG. 1.



Curves I, II, III, *and* IV *at* 100°, 90°, 80°, *and* 70°, *respectively.*

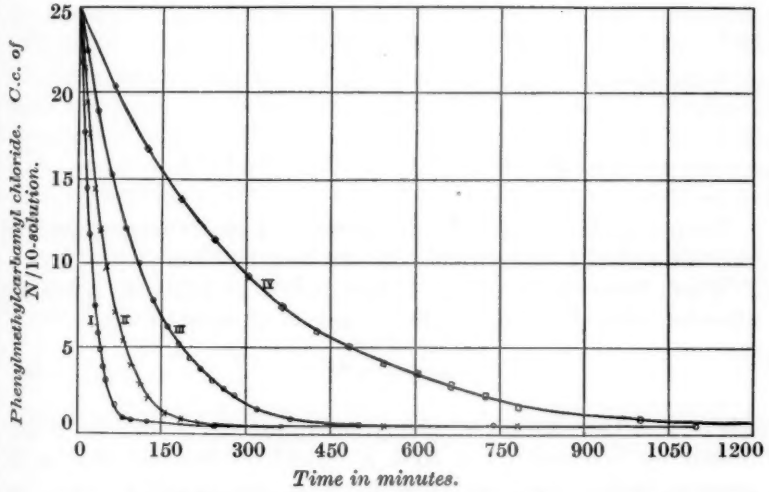
FIG. 2.

Fig. 2 shows the relation between the amount of ethyl chloride present and time at 100°, 90°, 80°, and 70°. At each temperature the curve has an inflexion, showing that the rate of formation of ethyl chloride is at first very slow, then it increases until the rate is a maximum, and then decreases until equilibrium is approached. As was to be expected, the point of inflexion corresponding to the

maximum speed of formation of ethyl chloride occurs when the amount of hydrogen chloride present is the maximum, and the very slow rates of formation are at the beginning and the end of the reaction, when there is very little hydrogen chloride present.

Fig. 3 shows the relation between the amount of phenylmethylcarbamyl chloride and time at the various temperatures. The curves are of the usual type obtained in a unimolecular reaction. The values obtained for the velocity coefficient of the first reaction, calculated, for a unimolecular reaction, from the amount of phenylmethylcarbamyl chloride present, are in good agreement at each temperature, until more than 90 per cent. of the carbamyl chloride has reacted.

FIG. 3.



Curves I, II, III, *and* IV *at* 100°, 90°, 80°, *and* 70°, *respectively.*

The amounts of the various substances present at any time can be calculated from a knowledge of the two separate velocity coefficients and the initial amount of carbamyl chloride. Thus, in the present case, if we represent phenylmethylcarbamyl chloride by A, hydrogen chloride by B, and ethyl chloride by C, we have two reactions, $A \longrightarrow B$, and $B \longrightarrow C$. If we start with a mols. of A and suppose that at a time t there are x mols. of A, y mols. of B, and z mols. of C present,

then $$x + y + z = a \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The rate of disappearance of A is $-dx/dt$

and $$-dx/dt = k_1 x \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where k_1 is the velocity coefficient of the transformation of A into B. From this,

$$x = ae^{-k_1 t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

which enables the amount of hydrogen chloride (x) to be calculated.

The rate of formation of C is

$$+ dz/dt = k_2 y \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where k_2 is the velocity coefficient for the transformation of B into C. The rate of accumulation of B in the system is

$$\begin{aligned} dy/dt &= -dx/dt - dz/dt \quad . \quad . \quad . \quad . \quad . \quad (5) \\ &= k_1 x - k_2 y \end{aligned}$$

and

$$dy/dt + k_2 y = k_1 a e^{-k_1 t} \quad . \quad . \quad . \quad . \quad (6)$$

from which, since when $t = 0$, $y = 0$,

$$y = a\left(\frac{k_1}{k_2 - k_1} e^{-k_1 t} + \frac{k_1}{k_1 - k_2} e^{-k_2 t}\right) \quad . \quad . \quad . \quad (7)$$

From equations (3) and (7), the amount of phenylmethylcarbamyl chloride and of hydrogen chloride can be calculated.

When, however, the actual "zero point" is taken as t_1 minutes after the time of mixing, we have, instead of equation (3),

$$x = p \,.\, e^{-k_1(t - t_1)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where p is the amount of phenylmethylcarbamyl chloride present (found by experiment) at time t_1, which is five minutes in the present work. Also, at time t_1, y is not equal to zero, but to a quantity q, which is found by experiment. Thus instead of equation (7) we get

$$y = \frac{pk_1 e^{k_1(t_1 - t)}}{k_2 - k_1} + \left(\frac{qk_2 - (p + q)k_1}{k_2 - k_1}\right) e^{k_2(t_1 - t)} \quad . \quad . \quad (9)$$

And

$$z = a - x - y \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Thus, by means of equations (8), (9), and (10) it is possible to calculate the amount of the three substances present at any time, taking any previous time as the "zero point."

The following table shows some of the observed and calculated values at 100°, where $k_1 = 0{\cdot}0426$ (obtained from section A), $k_2 = 0{\cdot}0102$ (obtained from section B), $p = 21{\cdot}93$, $q = 2{\cdot}54$, $a = 25{\cdot}0$, and $t_1 = 5$ mins. All the figures represent c.c. of $N/10$-solution.

Time (mins.).	HCl. Obs.	HCl. Calc.	Carbamyl chloride. Obs.	Carbamyl chloride. Calc.	Ethyl chloride. Obs.	Ethyl chloride. Calc.
5	2·54	—	21·93	—	0·53	—
10	6·39	6·55	17·74	17·72	0·87	0·63
15	9·46	9·50	14·43	14·32	1·11	1·18
30	14·44	14·37	7·56	7·56	3·00	3·07
40	15·55	15·46	4·87	4·94	4·58	4·60
45	15·57	15·61	3·81	3·99	5·62	5·40
50	15·38	15·58	3·22	3·22	6·40	6·20
80	13·40	13·42	0·95	0·90	10·65	10·68
125	10·27	9·06	0·80	0·13	13·93	15·81
365	2·41	0·80	0·46	0·00	22·13	24·20
1085	0·25	0·00	0·54	0·00	24·21	25·00

The agreement between theory and practice is satisfactory up to eighty minutes' heating; beyond that there is considerable divergence. The reason for this is twofold. First, the transformation of carbamyl chloride into hydrogen chloride is not complete and equilibrium is being attained after eighty minutes, and, secondly, the velocity coefficient k_2, as shown in section B, decreases steadily and the value employed for the purpose of the above calculation is only applicable to the first stages of the reaction between hydrogen chloride and ethyl alcohol. This stage does not last beyond eighty minutes in the above case.

It is also possible to calculate the maximum quantity of hydrogen chloride, since y will be a maximum when $dy/dt = 0$. From this it can be shown that

$$y_{max} = \frac{(pk_1/k_2)^{k_2/k_2-k_1}}{(p+q-qk_2/k_1)^{k_1/k_2-k_1}} \quad . \quad . \quad . \quad . \quad (11)$$

Equation (11) has been tested by using the appropriate values for p, q, k_1, and k_2 at 100°, 90°, 80°, and 70° with the following results :

Temp.		100°	90°	80°	70°
Max. value of y	Calc.	15·62	16·07	16·97	17·47
	Obs.	15·57	15·91	16·95	17·53

The time at which y is a maximum can be shown to be

$$t = \frac{1}{k_1 - k_2} \log \left(\frac{k_1}{k_2} \frac{(pk_1 e^{k_1 t_1})}{\{qk_2 + (p+q)k_1\} e^{k_2 t_1}} \right) \quad . \quad . \quad (12)$$

Substituting the appropriate values for k_1, k_2, p, q, and t_1 (= 5 mins. in each case), the times taken to reach the maximum amount of hydrogen chloride are as shown in the following table :

Temp.		100°	90°	80°	70°
Time (mins.)	Calc.	44·8	102·5	238·8	667·6
	Obs.	45	110	240	665

The agreement between the calculated and observed values for the maximum amount of hydrogen chloride present and the time

required for the production of this quantity is good at each temperature. A closer agreement would probably have been obtained if more observations had been taken in the neighbourhood of the maximum point. Thus, the expressions deduced for the calculation of (*a*) the amounts of the three substances present at any time, (*b*) the maximum amount of hydrogen chloride present, and (*c*) the time taken for this maximum to be reached, all give satisfactory representations of the experimental data.

These expressions enable any instant, and not only the time of mixing, to be taken as the starting point, thus obviating initial disturbances.

Effect of Temperature on the Velocity Coefficients.

The influence of temperature on velocity of reactions has received considerable attention in recent years, especially from the point of view of radiation. The fundamental equation representing the influence of temperature in terms of the radiation theory, due to Marcelin (*Compt. rend.*, 1914, **158**, 116, 407) and to Rice (*Rep. Brit. Assoc.*, 1915, 397), is

$$d \log k/dt = E/RT^2,$$

where E is the critical increment of internal energy which a molecule must receive before it can react, and R is the gas constant. On integration this gives

$$\log (k_{t_1}/k_{t_2}) = E(1/T_2 - 1/T_1),$$

which is of the same form as the well-known equation of Arrhenius.

Lewis (T., 1916, **109**, 796), applying Planck's radiation formula to this, states that "any agency which increases the reaction velocity (positive catalysis) diminishes the temperature coefficient of the constant : any agency which diminishes the velocity (negative catalysis) increases the value of the coefficient."

Cox (T., 1921, **119**, 144) points out that a special case of this and of the wider generalisation of Skrabal (*Monatsh.*, 1916, **37**, 495) is that the temperature coefficient will be inversely as the velocity in the presence of any given solvent or catalyst.

The reactions studied in the present communication are of interest in that in each case ethyl alcohol is both the solvent and one of the substances taking part in the reaction. The temperature coefficients are :

1st reaction : $k_{100°}/k_{90°} = 2{\cdot}173$; $k_{90°}/k_{80°} = 2{\cdot}245$; $k_{80°}/k_{70°} = 2{\cdot}653$.

2nd reaction : $k_{100°}/k_{90°} = 2{\cdot}303$; $k_{90°}/k_{80°} = 2{\cdot}735$; $k_{80°}/k_{75°} = 3{\cdot}109$.

The mean value of E, taking $R = 1{\cdot}985$ calories, is 1st reaction — 10,900 and 2nd reaction — 12,600.

When the velocity coefficient is plotted against the reciprocal of the absolute temperature, the resulting curve is a straight line for each reaction, showing the inverse proportionality. Thus it would appear that Lewis's deductions are correct.

The slope of the curve, which represents the variation of the temperature coefficient, is greater for the second reaction than for the first one, showing that the velocity of the second reaction decreases more rapidly with falling temperature than does that of the first reaction; thus the maximum amount of hydrogen chloride present in the system increases as the temperature falls.

Summary.

The reaction between phenylmethylcarbamyl chloride and ethyl alcohol has been studied in sealed tubes at 100°, 90°, 80°, and 70°. Under these conditions the whole reaction consists of two consecutive unimolecular reactions.

The velocity coefficients of the two reactions have been obtained independently, and from these were deduced expressions for the amounts of phenylmethylcarbamyl chloride, hydrogen chloride, and ethyl chloride present at any time, taking as the starting point, not the time of mixing, but any time during the course of the reaction.

The maximum amount of hydrogen chloride present and the time taken for this maximum to be reached were also deduced.

The results in all cases agreed satisfactorily with theory.

The variation of the velocity coefficients with temperature agrees with the deduction of Lewis based on the radiation hypothesis.

Further work is in progress using other carbamyl chlorides and other hydroxy-compounds.

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XVII.—*Piperitone. Part VII. The Constitution of Piperitone.*

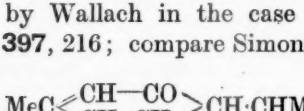
By JOHN READ, HENRY GEORGE SMITH, and REGINALD SLATER HUGHESDON.

IN the original paper of this series (T., 1921, **119**, 779), piperitone was accepted as a *p*-menthen-3-one; the evidence then available, however, seemed to indicate that this eucalyptus ketone was distinct from any known menthenone, and accordingly the further discussion of its constitution was reserved until the accumulation

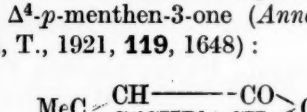
of further data. It was pointed out that the semicarbazone, the sole derivative upon which it was possible at the time to base comparisons, exhibited a close similarity to the semicarbazone of Wallach's synthetic Δ^1-*p*-menthen-3-one (*Annalen*, 1908, **362**, 272), whilst, on the other hand, piperitone appeared to be unique in the readiness with which it yielded a monobenzylidene derivative (*loc. cit.*, p. 782).

Subsequent studies of the oximes (T., 1922, **121**, 582) and semicarbazones (T., 1922, **121**, 1863) have served to establish convincingly the chemical identity of piperitone with (*a*) the optically inactive synthetic Δ^1-*p*-menthen-3-one of Wallach (*loc. cit.*), (*b*) the optically inactive ketone prepared from Japanese peppermint oil by Schimmel and Co. (*Semi-Annual Report*, 1910, 97), (*c*) the optically inactive ketone isolated by Roberts from the essential oil of *Cymbopogon sennaarensis* (T., 1915, **107**, 1466), and (*d*) the dextrorotatory ketone extracted from the essential oil of *Andropogon Jwarancusa* by Simonsen (T., 1921, **119**, 1644).

In considering the question of the constitution of piperitone, it is of interest to remark that, apart from its identity with Wallach's synthetic Δ^1-*p*-menthen-3-one, the evidence bearing upon the position of the ethylenic linking has accrued from a study of the oxidation products of the naturally occurring ketone. Thus, in the first instance, Schimmel and Co. (*loc. cit.*), by disruptive oxidation of the ketone from Japanese peppermint oil, prepared α-hydroxy-α-methyl-α′-*iso*propyladipic acid, γ-acetyl-α-*iso*propylbutyric acid, and α-*iso*propylglutaric acid, whilst Roberts (*loc. cit.*), in addition to the first-named acid, obtained diosphenol by oxidising the ketone from the oil of *C. sennaarensis*. Similar results were obtained by Simonsen (*loc. cit.*) on applying the oxidative method to *d*-piperitone from the oil of *A. Jwarancusa*. The analytical and synthetical data are thus in accordance, and indicate the identity of piperitone with Δ^1-*p*-menthen-3-one (I). The ready production of a benzylidene derivative (II) is then explained by the activation of carbon atom 6, owing to its proximity to the ethylenic linking, a similar activation of the same carbon atom having been recorded by Wallach in the case of Δ^4-*p*-menthen-3-one (*Annalen*, 1913, **397**, 216; compare Simonsen, T., 1921, **119**, 1648):



(I.)



(II.)

In view of the notable ease with which isomerisation may precede oxidative breakdown in the case of unsaturated substances, it appeared desirable, however, to confirm the above conclusions

respecting the position of the ethylenic linking in the piperitone molecule by the application of less violent methods; a procedure was accordingly devised which utilised the application of mild reagents at the ordinary temperature and involved no rupture of the ring system. The acceptance of the structure of a *p*-menthen-3-one for piperitone, which, moreover, affords no indication of unsaturation in the side-chains, limits the possible positions of the ethylenic linking to four, namely, Δ^1, Δ^4, Δ^5, and Δ^6; and, of these, the second corresponds with a known ketone distinct from piperitone (Wallach, *loc. cit.*), whilst the ready racemisation of *d*- and *l*-piperitone in the presence of alkali points to carbon atom 4 as the sole asymmetric atom in the molecule. Of the remaining theoretical possibilities, the Δ^5- and Δ^6-ketones should yield a 2-benzylidene derivative upon reacting with benzaldehyde, whilst the Δ^1-ketone could only yield a 6-benzylidene derivative in such a circumstance, as explained above. Upon hydrogenation, the benzylidene derivative from either the Δ^5- or the Δ^6-ketone would pass into 2-benzylmenthone (III), whilst the benzylidene derivative from the Δ^1-ketone would furnish 6-benzylmenthone (IV). The original piperitone, on the other hand, when hydrogenated prior to treatment with benzaldehyde, would yield 2-benzylidenementhone, which, upon subsequent further hydrogenation, would pass into 2-benzylmenthone (III):

(III.) $$\mathrm{MeCH}\begin{<}\mathrm{CH(CH_2Ph)\cdot CO}\\ \mathrm{CH_2}\text{———}\mathrm{CH_2}\end{>}\mathrm{CH\cdot CHMe_2}$$

(IV.) $$\mathrm{MeCH}\begin{<}\mathrm{CH_2}\text{———}\mathrm{CO}\\ \mathrm{CH(CH_2Ph)\cdot CH_2}\end{>}\mathrm{CH\cdot CHMe_2}.$$

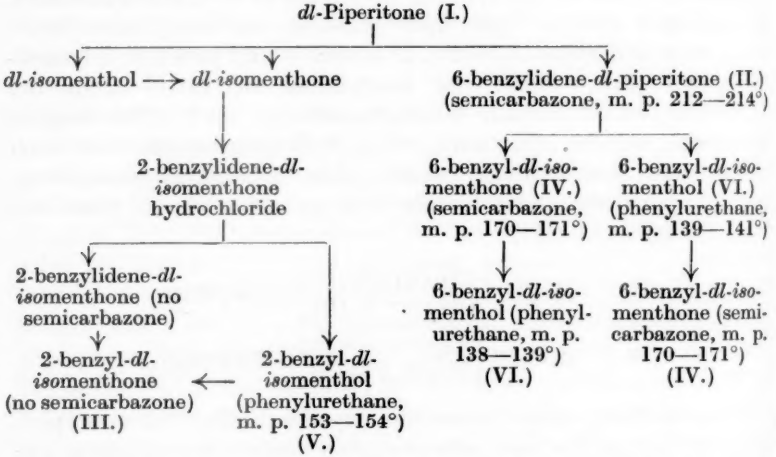
Upon realising these operations experimentally, the two specimens of benzylmenthone prepared from *dl*-piperitone in these two ways proved to be distinct; consequently, the constitution Δ^1-*p*-menthen-3-one for piperitone is confirmed, and benzylidenepiperitone is to be identified with 6-benzylidene-Δ^1-*p*-menthen-3-one. The ketone (IV) prepared by hydrogenating the last-named derivative gave a characteristic semicarbazone melting at 170—171°, whereas the isomeric ketone (III) failed to react with semicarbazide; this interesting distinction is probably to be referred to spacial considerations and thus provides a further confirmation of the relative positions of the groups. In view of recent investigations (T., 1923, **123**, 2196) on the hydrogenation of piperitone, the derivatives referred to in this communication should probably be regarded as derived from *iso*menthone rather than from menthone. It may be noted, moreover, that each of the above benzyl-*dl*-*iso*menthones (III and IV) possibly consists of a mixture of stereo-

isomerides, owing to the production of two new asymmetric carbon atoms during the process of synthesis from *dl*-piperitone. The benzyl*iso*menthols (V and VI) obtained by reducing these ketones also exhibited pronouncedly different characteristics; they yielded distinct phenylurethanes, whilst in the case of 6-benzyl-*dl-iso*menthol only (VI), a solid component was isolated, melting at 66—68°:

(V.) $MeCH<^{CH(CH_2Ph)\cdot CH(OH)}_{CH_2\text{———}CH_2}>CH\cdot CHMe_2$

(VI.) $MeCH<^{CH_2\text{——}CH(OH)}_{CH(CH_2Ph)\cdot CH_2}>CH\cdot CHMe_2$

From the appended summary of the relationships involved, it will be seen that three out of the four derivatives selected for comparison were prepared in two ways:


dl-Piperitone (I.)
*dl-iso*menthol
*dl-iso*menthone
6-benzylidene-*dl*-piperitone (II.) (semicarbazone, m. p. 212—214°)
2-benzylidene-*dl-iso*menthone hydrochloride
6-benzyl-*dl-iso*menthone (IV.) (semicarbazone, m. p. 170—171°)
6-benzyl-*dl-iso*menthol (VI.) (phenylurethane, m. p. 139—141°)
2-benzylidene-*dl-iso*menthone (no semicarbazone)
6-benzyl-*dl-iso*menthol (phenylurethane, m. p. 138—139°) (VI.)
6-benzyl-*dl-iso*menthone (semicarbazone, m. p. 170—171°) (IV.)
2-benzyl-*dl-iso*menthone (no semicarbazone) (III.)
2-benzyl-*dl-iso*menthol (phenylurethane, m. p. 153—154°) (V.)

As a final confirmation of the arguments advanced above, it may be added that 6-benzyl-*dl-iso*menthone proved to be capable of reacting anew with benzaldehyde to form 2-benzylidene-6-benzyl-*dl-iso*menthone, whilst 2-benzyl-*dl-iso*menthone was incapable of so reacting.

Attention has already been directed to the fact that with the single exception of *Eucalyptus apiculata* piperitone invariably occurs in eucalyptus oils in association with *l*-α-phellandrene, and that in most instances it also appears to be accompanied by the corresponding secondary alcohol, piperitol. The relationship of the $\Delta^{2\cdot6}$-conjugated system of *l*-α-phellandrene with the intermediate Δ^{1}-linking of *l*-piperitol and *l*-piperitone is thus particularly suggestive in connexion with the natural association of these three substances (compare T., 1921, **119**, 781).

EXPERIMENTAL.

2-*Derivatives of* dl-iso*Menthone*.

2-*Benzylidene*-dl-iso*menthone Hydrochloride*, $C_{10}H_{16}O{:}CHPh,HCl$.—*dl-iso*Menthol, obtained by reducing pure *dl*-piperitone with sodium and alcohol, was oxidised by means of chromic acid to *dl-iso*menthone, in the way described recently (T., 1923, **123**, 2919). *dl-iso*Menthone (46 grams) was then condensed in the presence of dry hydrogen chloride with benzaldehyde (31·4 grams), the gas being passed into the cooled mixture for about two hours, until saturation was complete. Upon keeping the mixture over-night in the ice-chest, a semi-solid mass resulted. After trituration with a slight excess of sodium hydroxide solution, the material was rendered faintly acid and then freed from unchanged benzaldehyde or *iso*menthone by steam distillation. The purified product was moderately soluble in hot methylated spirit, from which it crystallised on cooling in fine, colourless needles (24 grams), m. p. 108—110°. One recrystallisation sufficed to raise the melting point to 119—120° (Found : C = 72·59; H = 8·33. $C_{17}H_{23}OCl$ requires C = 73·21; H = 8·32 per cent.).

From the mother-liquors of the above substance was obtained a small quantity (1·5 grams) of an isomeric 2-*benzylidene*-dl-iso*menthone hydrochloride*, which formed colourless, glistening needles, m. p. 129—130° (Found : C = 73·30; H = 8·45 per cent.).

The remainder of the mother-liquors, when freed from alcohol and distilled under diminished pressure, yielded a first fraction (7 grams) which distilled at 185—195°/17 mm. and crystallised on cooling, and a second fraction (27 grams) which distilled at 195—203°/17 mm. and formed a greenish-yellow liquid. Both the crystalline and the liquid preparations yielded the same 2-benzylidene-*dl-iso*menthone when treated with alcoholic sodium ethoxide, and consequently for the preparation of the latter derivative or of 2-benzyl-*dl-iso*menthol it is sufficient to purify the crude 2-benzylidene-*dl-iso*menthone hydrochloride by steam distillation alone.

*dl-iso*Menthone prepared directly from *dl*-piperitone by catalytic hydrogenation in the presence of colloidal palladium (T., 1923, **123**, 2921) gave a similar result.

2-*Benzyl*-dl-iso*menthol*, $C_{10}H_{19}O{\cdot}CH_2Ph$.—2-Benzylidene-*dl-iso*menthone hydrochloride (15 grams) was dissolved in absolute alcohol (140 c.c.) and reduced with sodium (14 grams). The resulting 2-benzyl-*dl-iso*menthol distilled at 194—196°/20 mm. as a colourless and very viscid liquid. When warmed on the water-bath with phenylcarbimide, it yielded a *phenylurethane*, which after recrystallisation from benzene and light petroleum melted at 153—154°

(Found: C = 78·44; H = 8·59. $C_{24}H_{31}O_2N$ requires C = 78·88; H = 8·58 per cent.).

2-*Benzylidene*-dl-iso*menthone*, $C_{10}H_{16}O{:}CHPh$.—2-Benzylidene-*dl-iso*menthone hydrochloride (11·6 grams) was boiled under reflux for twenty minutes with alcohol (120 c.c.) in which sodium (1·8 grams) had been previously dissolved. The alcohol was then removed by steam distillation, and by extraction with ether and eventual distillation under diminished pressure 2-benzylidene-*dl-iso*menthone was obtained in 86 per cent. yield as a colourless liquid boiling at 193—195°/15 mm. Attempts to prepare a semicarbazone of this ketone were unsuccessful.

2-*Benzyl*-dl-iso*menthone*, $C_{10}H_{17}O{\cdot}CH_2Ph$.—2-Benzylidene-*dl-iso*menthone (45 grams) was dissolved in pure ether (50 c.c.) and hydrogenated at the ordinary temperature under a pressure of one atmosphere, in contact with a solution of palladium chloride (0·3 gram) and gum arabic (0·5 gram) in water (200 c.c.). The mixture was stirred vigorously for three hours, after which the absorption of hydrogen was complete. 2-Benzyl-*dl-iso*menthone was obtained in 80 per cent. yield as a pale yellow, viscid liquid, b. p. 195—197°/20 mm., having $d_{4^\circ}^{20^\circ}$ (vac.) 0·9957, n_D^{20} 1·5230, and $[R_L]_D$ 74·92 (calc. value, 75·15) (Found: C = 83·46; H = 9·73. $C_{17}H_{24}O$ requires C = 83·55; H = 9·90 per cent.).

A specimen of the same substance derived, in 80 per cent. yield, by the oxidation of 2-benzyl-*dl-iso*menthol with chromic acid, distilled at 192—195°/19 mm., and had $d_{4^\circ}^{20^\circ}$ (vac.) 0·9846, $n_D^{20^\circ}$ 1·5159, and $[R_L]_D$ 74·90.

Attempts to prepare a semicarbazone or an oxime from the ketone were unsuccessful, whilst it also failed to react with benzaldehyde in the presence of dry hydrogen chloride.

6-*Derivatives of* dl-iso*Menthone*.

6-*Benzylidene*-dl-*piperitone*, $C_{10}H_{14}O{:}CHPh$.—This derivative, prepared in the manner already described (T., 1921, **119**, 785), readily yielded a *semicarbazone* when allowed to react with semicarbazide hydrochloride and sodium acetate under the conditions defined in a previous paper (T., 1922, **121**, 1867). The substance was only slightly soluble in boiling alcohol, but from hot chloroform it was obtained in clusters of minute, colourless needles, m. p. 212—214°. Solutions in alcohol and chloroform were pale yellow, and the solid substance rapidly assumed a canary-yellow colour when dried (compare T., 1921, **119**, 789). Warm dilute hydrochloric acid dissolved the substance, and it was reprecipitated unchanged upon neutralising the resulting deep yellow solution. The derivative retained a molecular proportion of water, even

after recrystallisation from chloroform (Found: C = 68·79; H = 7·75; loss at 120° = 5·77. $C_{18}H_{23}ON_3 + H_2O$ requires C = 68·56; H = 7·99; H_2O = 5·71 per cent.). No isomeric semicarbazone was produced in this instance.

6-*Benzyl*-dl-iso*menthone*, $C_{10}H_{17}O{\cdot}CH_2Ph$.—6-Benzylidene-*dl*-piperitone (20 grams) was dissolved in pure ether (100 c.c.) and thoroughly emulsified, as described above, with a solution of palladium chloride (0·3 gram) and gum arabic (0·5 gram) in water (150 c.c.). Upon admitting hydrogen at the ordinary temperature under a pressure of 0·5 atmosphere, the calculated volume was absorbed in two hours. From the product, 6-benzyl-*dl-iso*menthone was readily isolated, in 87 per cent. yield, in the form of a colourless, viscid liquid with a faint, pleasant odour; it distilled at 202—203°/14 mm., and had $d_4^{20°}$ (vac.) 0·9884, $n_D^{20°}$ 1·5176, and $[R_L]_D$ 74·84 (calc. value, 75·15). The ketone did not decolorise hot dilute potassium permanganate solution, but when dissolved in chloroform it absorbed bromine readily in the cold. Benzylidene-*dl*-piperitone, on the other hand, was readily oxidised by hot dilute potassium permanganate, with the production of benzaldehyde.

When treated at the ordinary temperature with semicarbazide hydrochloride and sodium acetate in the usual way, 6-benzyl-*dl-iso*menthone readily yielded a *semicarbazone*, which separated from hot alcohol in aggregates of minute, transparent, colourless prisms, m. p. 170—171° (Found: C = 71·41, 71·38; H = 8·98, 9·01. $C_{18}H_{27}ON_3$ requires C = 71·66; H = 9·09 per cent.).

From the mother-liquors was isolated a small amount of a very soluble isomeric *semicarbazone*, which was deposited from warm light petroleum in clusters of woolly needles, melting rather indefinitely at about 95° (Found: C = 71·47; H = 9·30 per cent.).

6-Benzyl-*dl-iso*menthone was also prepared by oxidising 6-benzyl-*dl-iso*menthol (26 grams) with chromic acid, according to the method described by Beckmann for oxidising *l*-menthol (*Annalen*, 1889, **250**, 325), the 6-benzyl-*dl-iso*menthol being obtained by reducing 6-benzylidene-*dl*-piperitone with sodium and alcohol, as indicated below. The product (16 grams) distilled at 213—220°/20 mm., and had $d_4^{20°}$ (vac.) 0·9905, $n_D^{20°}$ 1·5239, and $[R_L]_D$ 75·42. A semicarbazone was readily isolated which melted at 170—171° when heated alone or in admixture with the semicarbazone of the same melting point described above.

6-Benzyl-*dl-iso*menthone reacted with benzaldehyde in the presence of dry hydrogen chloride to yield 2-*benzylidene*-6-*benzyl*-dl-iso*menthone hydrochloride*, $C_{24}H_{29}OCl$. The greater part of the product remained as a viscid liquid, but a small quantity of fine,

colourless needles melting with decomposition at 202—203° was isolated. By treatment with alcoholic sodium ethoxide, the mixed product furnished, in 60 per cent. yield, 2-*benzylidene*-6-*benzyl*-dl-iso*menthone*, $C_{24}H_{28}O$, which formed a pale yellow, mobile oil distilling at 218—225°/15 mm. Reduction of the latter product with sodium and alcohol yielded 2 : 6-*dibenzyl*-dl-iso*menthol*, $C_{24}H_{32}O$, a pale yellow and very viscid liquid, which distilled at 282—287°/23 mm.

6-*Benzyl*-dl-iso*menthol*, $C_{10}H_{19}O{\cdot}CH_2Ph$.—When reduced rapidly with sodium and alcohol in the usual way, 6-benzyl-*dl-iso*menthone, obtained from 6-benzylidene-*dl*-piperitone by catalytic hydrogenation, readily afforded 6-benzyl-*dl-iso*menthol in 90 per cent. yield. It distilled at 203—207°/16 mm., and was somewhat less viscid than 2-benzyl-*dl-iso*menthol, described above. The substance also distilled at about 350°/760 mm., without noticeable decomposition. The *phenylurethane* crystallised from a mixture of light petroleum and benzene in colourless, feathery needles, m. p. 138—139° (Found : C = 78·81; H = 8·85. $C_{24}H_{31}O_2N$ requires C = 78·88; H = 8·58 per cent.).

A careful direct comparison showed that 6-benzyl-*dl-iso*menthol, prepared in the way described above, was identical with the supposed " benzyl-*p*-menthenol " previously obtained by the direct reduction of 6-benzylidene-*dl*-piperitone with sodium and alcohol (T., 1922, **121**, 581). Various specimens of the phenylurethane derived from such preparations melted at temperatures between 139° and 141°, and admixture with the phenylurethane described above produced no appreciable depression of the melting point. 6-Benzyl-*dl-iso*menthol prepared by either method readily absorbed bromine in chloroform solution at the ordinary temperature, but similar behaviour was exhibited by other saturated derivatives described in this paper, as also by *l*-menthol, etc., under similar conditions. Furthermore, attempts to reduce the supposed " benzyl-*p*-menthenol " by catalytic hydrogenation resulted in no absorption of hydrogen.

A further specimen of 6-benzyl-*dl-iso*menthol, prepared by reducing 6-benzylidene-*dl*-piperitone with sodium and alcohol, distilled at 203—207°/16 mm., and when kept for three weeks at the ordinary temperature became partly crystalline. After two days' further keeping in the ice-chest, the preparation (12 grams) yielded a quantity of fine, colourless needles (2·5 grams), which when pressed on a porous plate and recrystallised from light petroleum melted at 66—68° (Found : C = 82·95; H = 10·44. $C_{17}H_{26}O$ requires C = 82·85; H = 10·64 per cent.). The phenylurethane yielded by this crystalline 6-*benzyl*-dl-iso*menthol* melted

at 139—140°, and exhibited no depression of melting point when mixed with the similar preparation described above.

Mixtures of 6-benzyl-*dl-iso*menthol phenylurethane (m. p. 139—141°) and 2-benzyl-*dl-iso*menthol phenylurethane (m. p. 153—154°) melted at 126—128°, thus confirming the distinction between these two isomeric benzyl-*dl-iso*menthols derived in different ways from *dl*-piperitone.

We have pleasure in acknowledging our indebtedness to the McCaughey Research Fund of the University of Sydney for a grant in aid of these investigations, which are being continued.

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XVIII.—*The System Antimonious Oxide–Hydrochloric Acid–Water.*

By CHARLES LEA and JOHN KERFOOT WOOD.

IN continuation of the investigation of the behaviour of amphoteric metallic hydroxides (T., 1908, **93**, 411; 1910, **97**, 878; 1916, **109**, 164), the authors commenced experiments on the action of solutions of hydrochloric acid and of sodium hydroxide upon hydrated antimonious oxide. As the work on the action of hydrochloric acid proceeded, it appeared desirable to extend the field of investigation so as to study the action of water on antimonious chloride, and the conditions governing the formation of the various oxychlorides of antimony; the results obtained from these latter lines of inquiry form the material of the present communication, those obtained from the examination of alkaline solutions being reserved for a future paper.

Determinations of the solubility of antimonious oxide in hydrochloric acid were made by Causse (*Compt. rend.*, 1892, **113**, 1042), the amount of oxide dissolved by a known volume of acid being found from the difference between the weight of oxide taken and that of the undissolved substance. As the method takes no account of the fact that the undissolved material would consist, not of the oxide, but of an oxychloride, the results obtained cannot be regarded as trustworthy.

Numerous workers have studied the action of water on antimonious chloride, the earliest trustworthy information being

obtained by Sabanajew (*Z. Chem.*, 1871, **7**, 204). He observed that the nature of the result depended on the relative amounts of the two substances employed. On the addition of 2 mols. of water to 1 mol. of the solid trichloride, the latter substance dissolved and could be recovered unchanged by evaporating the solution, but where larger quantities of water were employed the trichloride suffered decomposition and yielded various oxychlorides. Compounds having the formulæ SbOCl and $Sb_4O_5Cl_2$ were obtained by the addition of 8 and 27 mols. of water, respectively, to 1 mol. of antimonious chloride; on the addition of still larger quantities of water, amorphous products containing smaller proportions of chlorine, and considered to be mixtures of antimonious oxide and $Sb_4O_5Cl_2$, were obtained, but the complete removal of the chlorine could be brought about only by prolonged washing with very large volumes of water. The point at which the precipitate of oxychloride changed in composition from SbOCl to $Sb_4O_5Cl_2$ appeared to be where the free acid in the solution had a concentration of about 2·5*N*, whilst that at which the latter compound began to change into oxide corresponded to a concentration of 0·25*N*. Le Chatelier (*Compt. rend.*, 1885, **100**, 737) arrived at a somewhat similar result regarding the former transition point, and stated that when the free hydrochloric acid exceeds 70 grams per litre the precipitate obtained at 15° consists of SbOCl, whilst below the concentration mentioned the substance has the composition $Sb_4O_5Cl_2$; the total chlorine concentration of the solution at the transition point was 2·12*N*. As will be shown later, the authors' experiments have demonstrated that both the transition points quoted are incorrect, the oxychloride having the composition $Sb_4O_5Cl_2$ being stable in contact with solutions of hydrochloric acid covering a much wider range of concentration; the point at which SbOCl undergoes conversion into $Sb_4O_5Cl_2$ corresponds to a total chlorine concentration of about 8·0*N*, whilst the transition from antimonious oxide takes place when the chlorine concentration of the solution is in the neighbourhood of 0·1*N*. The error made in the earlier determinations appears to be due to the formation of metastable products which are only very slowly transformed into the stable solid phase.

Van Bemmelen and his collaborators (*Z. anorg. Chem.*, 1903, **33**, 272) reported that a new oxychloride, referred to as "X," was deposited from solutions prepared by the addition of from 1·38 to 4 mols. of water to 1 mol. of antimonious chloride. The composition of the substance was not definitely established, but it was supposed to be a compound of antimonious chloride and the oxychloride SbOCl; it would appear, however, that the substance

really consists of the above oxychloride in a distorted, crystalline form.

Numerous references to an amorphous form of the oxychloride SbOCl are found in the literature, but the authors' experiments indicate that this is really an adsorption product formed by freshly precipitated hydrated antimonious oxide taking up hydrochloric acid from the solution. The adsorption product differs in composition according to the concentration of the solution with which it is in contact, and suffers transformation into various crystalline oxychlorides, two of the latter also being metastable; amongst the latter is a substance having the formula $Sb_4O_3(OH)_5Cl$, which appears to be identical with a crystalline product obtained by Cooke (*Proc. Amer. Acad.*, 1886, **13**, 1). The other metastable oxychloride which appears to be formed under certain conditions probably has the formula $Sb_4O_3(OH)_3Cl_3$; the stable phases ultimately formed are SbOCl and $Sb_4O_5Cl_2$.

Experimental.

Action of Hydrochloric Acid on Hydrated Antimonious Oxide.

Hydrated antimonious oxide in a fine state of division was prepared by the action of ammonia on antimonious chloride (T., 1923, **123**, 264). Solutions of pure hydrochloric acid of varying concentration were prepared and the hydrated oxide was added in quantity more than sufficient to saturate the liquid, the flasks containing the mixtures being then securely corked and placed in a thermostat at 25°. After about two months, during which period the mixtures were shaken from time to time, portions of the solutions were removed for analysis, the remainder of the mixture in every case being left in the thermostat for another month, after which the composition was again determined; the results of the second analysis were in agreement with the earlier figures, thus indicating that the mixtures had attained equilibrium.

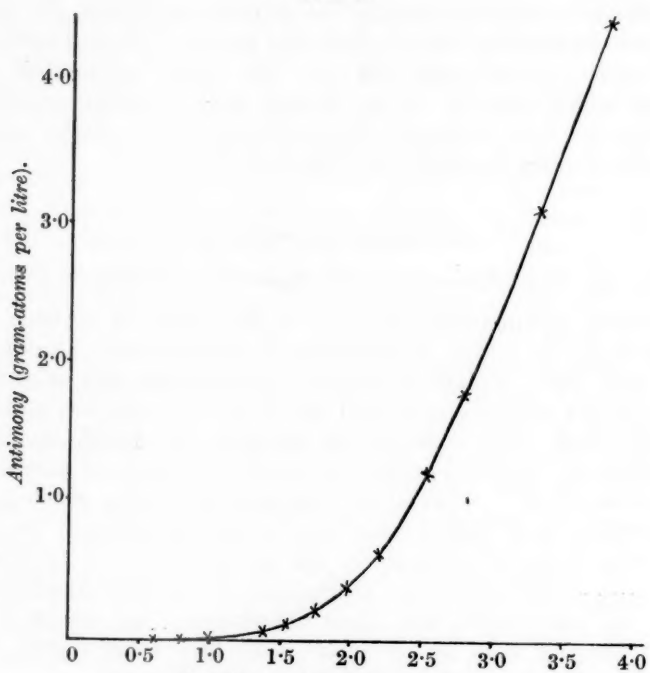
The total chlorine in the solution was estimated by titration with sodium hydroxide, with phenolphthalein as indicator. In those solutions having a concentration greater than 1·5*N* a better end-point was obtained by adding an excess of standard alkali and titrating back with acid. The neutral mixture was then employed for the determination of antimony, the precipitate of hydrated oxide being dissolved in tartaric acid solution; sodium hydroxide was added until the liquid was only faintly acid, after which an excess of sodium bicarbonate solution was added and the mixture titrated with iodine. Some of the results obtained are shown in Table I, the chlorine and antimony both being expressed in gram-

atoms per litre; these results were confirmed by those obtained from other solutions.

TABLE I.

Cl	0·198	0·402	0·601	0·799	1·02	1·32
Sb	0·00012	0·000172	0·000298	0·000610	0·00124	0·00565
Cl	1·56	1·74	1·90	2·10	2·29	2·54
Sb	0·0116	0·0194	0·0299	0·0522	0·0755	0·120
Cl	2·81	3·36	3·85	4·79	5·93	
Sb	0·177	0·309	0·440	0·745	1·13	

FIG. 1.



The results quoted fall on a perfectly smooth curve (Fig. 1), thus indicating the absence of a transition point in the region investigated. In view of the statements of previous investigators, a large number of mixtures containing between 1·5 and 2·5 gram-atoms of chlorine per litre were prepared and examined, but no evidence to suggest the existence of a transition point in this region could be obtained.

The hydrated oxide when added was in an extremely fine state of division, and remained suspended for a considerable time on shaking the mixture. After some time, however, it was observed

that the undissolved solid settled rapidly after shaking and in the more concentrated mixtures had a distinctly crystalline appearance. Some of the undissolved solid was removed, washed with a little alcohol and ether, dried, and analysed (Found : Sb = 76·10; Cl = 11·18. $Sb_4O_5Cl_2$ requires Sb = 76·11; Cl = 11·22 per cent.).

Action of Water on Antimonious Chloride.

The previously described experiments having failed to show the existence of a transition point in the region mentioned by earlier workers, it was decided to investigate the matter from the opposite direction and to examine the action of water on antimonious chloride. In all cases a bulky, white precipitate, assumed by former workers to consist of SbOCl, was first obtained on mixing the redistilled chloride with water. When sufficient water was added to bring the concentration of chlorine in the final liquid to about 2·2*N*, the precipitate changed fairly rapidly to a fine, crystalline powder, but when the dilution was somewhat less the transformation occurred more slowly. The crystalline substance on analysis was found to consist of the oxychloride $Sb_4O_5Cl_2$. An attempt was made to determine the composition of the bulky, white precipitate and for this purpose antimonious chloride was dissolved in a little water and the mixture diluted so as to bring the final chlorine concentration between 2·0*N* and 2·5*N*. After vigorously shaking the mixture for a minute, the precipitate was removed by filtration through a Buchner funnel, thoroughly drained, and dried on tile in a desiccator until of constant weight. The following results were obtained :

	Final chlorine concentration of liquid.	
	2·0*N*.	2·5*N*.
Antimony	74·8 per cent.	69·8 per cent.
Chlorine	11·7 „	15·3 „

$Sb_4O_5Cl_2$ requires Sb = 76·1 per cent. and Cl = 11·2 per cent., whilst SbOCl requires Sb = 70·0 per cent. and Cl = 20·7 per cent.

Not only did the two precipitates differ in composition, but in neither case did the analytical results correspond with the requirements of either of the oxychlorides. A microscopic examination of the dried precipitate showed the complete absence of crystals either of SbOCl or $Sb_4O_5Cl_2$; a further reference to this precipitate will be made later in the paper.

The mixture of amorphous precipitate and liquid changed on standing, crystals of $Sb_4O_5Cl_2$ gradually making their appearance until eventually the whole of the solid was converted into that compound; at the same time, the composition of the liquid underwent a change, until finally it corresponded with a point on the curve shown in Fig. 1.

As a result of the foregoing experiments, it appeared that the transition point of the two oxychlorides must correspond to a much higher concentration than was formerly thought to be the case, and therefore the action of water on concentrated solutions of antimonious chloride was examined. The solid chloride was dissolved in a small quantity of hydrochloric acid and water added until a permanent opalescence was obtained; after a few minutes a large amount of an amorphous precipitate appeared and several days later crystals began to form. On heating the mixture, the precipitate dissolved and, on cooling slowly, a crystalline deposit was obtained. Various mixtures were prepared in the manner described, and were left in the thermostat to attain equilibrium.

Special precautions were necessary in the analysis of these mixtures, partly because of the hygroscopic nature of the liquids, their liability to suffer atmospheric oxidation, and their high concentration. About 2 c.c. of the liquid were weighed in a small tared weighing bottle, pure tartaric acid was added and the whole was diluted to 250 c.c. The antimony in the diluted solution was estimated by means of $N/20$ iodine solution and the chlorine by the Volhard method, the percentage of the two elements in the original liquid then being calculated. After an interval of two weeks the analysis was repeated and if no change of composition had taken place the liquid was removed and the solid examined; the crystals of the latter were well washed with ether in order to free them completely from adhering liquid and were then dried in the desiccator and analysed. Some of the results obtained are given in Table II:

TABLE II.

	Liquid.		Solid.			Liquid.		Solid.	
	Antimony.	Chlorine.	Antimony.	Chlorine.		Antimony.	Chlorine.	Antimony.	Chlorine.
1	44·0	41·9	69·9	20·7	9	16·2	21·4	Mixture of crystals	
2	39·4	38·8	70·0	20·6					
3	33·0	34·5	69·8	20·7	10	14·8	20·7	—	11·3
4	28·7	31·6	70·0	20·6	11	11·3	17·5	76·1	11·2
5	27·1	30·4	69·9	20·6	12	7·5	14·3	76·1	11·2
6	23·8	27·9	70·1	20·7	13	4·5	11·7	76·1	11·3
7	21·2	25·8	70·0	20·7	14	1·9	9·0	76·0	11·1
8	18·7	23·7	—	20·7	15	1·7	8·9	76·2	11·2

It is obvious that the crystals which separated were of two kinds, the analyses indicating that the solid phase in the more concentrated mixtures consisted of SbOCl, whilst in the more dilute mixtures it was $Sb_4O_5Cl_2$. The two types of crystals are easily distinguishable from each other and both were seen to be present in the solid deposited from mixture 9. It would appear, therefore, that the point at which the solid phase changes from SbOCl to $Sb_4O_5Cl_2$

corresponds to a solution containing approximately 21·4 per cent. by weight of chlorine, that is, a solution having a chlorine concentration of about 8*N*.

An attempt was made to determine the composition of the substance "X" which van Bemmelen obtained on mixing antimonious chloride with less than 2½ molecular proportions of water and of which he had been unable to obtain a satisfactory analysis. Redistilled antimony chloride was mixed with 2 mols. of water and the mixture, after being well shaken, was left in the thermostat. A crystalline precipitate was obtained within a week and, no further change being observed during the succeeding two months, the liquid was poured off, the crystals were washed several times with ether, drained, dried in the desiccator, and analysed; the results obtained showed the crystals to consist of the oxychloride SbOCl. In appearance, the crystals differ from the ordinary crystals of SbOCl, being of the nature of prisms with pointed ends, whereas the substance usually crystallises in cubes; it has, however, been observed by the authors that there is a tendency for the crystals of SbOCl deposited from solutions of high concentration to present an elongated or distorted form, and it is probable that the form of van Bemmelen's product is to be accounted for in this way.

It is known that by treatment of $Sb_4O_5Cl_2$ with large quantities of water it is possible to remove the whole of the chlorine, so that in a certain region of concentration the oxide must be the stable solid phase. Sabanajew (*loc. cit.*) stated that no oxychloride is formed if the chlorine concentration of the solution is less than 0·25*N*, but experiments made by the authors show that $Sb_4O_5Cl_2$ is slowly formed when hydrated antimonious oxide is left in contact with 0·125*N*-hydrochloric acid. It is possible that the same substance may be formed by the action of an even more dilute solution of acid, but it is practically impossible to determine the point at which $Sb_4O_5Cl_2$ ceases to be the stable solid phase owing to the extreme slowness with which hydrated antimonious oxide is attacked by very dilute solutions of hydrochloric acid. It was thought the equilibrium in such solutions might be established more quickly by approaching from the other side, and therefore a solution of antimonious oxide in moderately concentrated hydrochloric acid was diluted with water so as to bring the final chlorine concentration slightly below decinormal. After standing for several days, beautiful, needle-shaped crystals began to form in clusters round the edge of the amorphous substance which had been previously deposited; the crystals increased in quantity, whereas the amorphous product gradually disappeared. The

crystals appeared to correspond with those previously obtained by Cooke (*loc. cit.*). The crystalline compound was removed, washed with alcohol and ether, dried, and analysed, but the results obtained from different preparations showed considerable variations with regard both to the antimony and the chlorine present. To the naked eye the products obtained from different preparations appeared similar and perfectly homogeneous, but on submitting them to a careful microscopical examination it was found that the needle-shaped crystals were invariably mixed with a certain quantity of amorphous matter; in addition, the products deposited from the more concentrated solutions contained some crystals of $Sb_4O_5Cl_2$, whilst occasional octahedra, consisting probably of antimonious oxide, were to be seen in the substance deposited from the more dilute solutions; the variation in the analytical results is thus easily accounted for.

In the hope of throwing further light on the reaction and definitely establishing the composition of the crystals, experiments of a similar nature were carried out under varying conditions. When the original concentrated solution was mixed with boiling water equal in volume to the cold water originally used, the reaction appeared to take place very quickly and to be complete in a few minutes. The product, however, was a cream-coloured powder and contained no needles; on cooling, an additional quantity of the powder was deposited, together with a few small needles. The composition of the solid matter varied according to the chlorine concentration of the final solution, as is indicated in the following table:

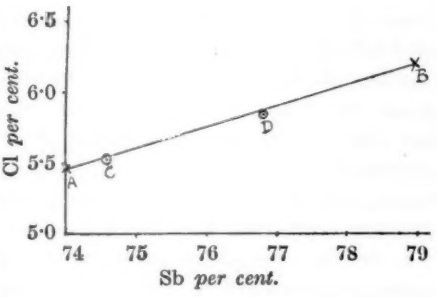
	1	2	3	4	5	6
% Cl in solid	3·0	5·53	6·03	6·12	6·19	8·46
Cl in solution (in normalities)	0·013	0·035	0·099	0·151	0·208	0·246

The above figures when plotted give a curve approximating in form to an adsorption isotherm until the chlorine in solution reaches a concentration of 0·22*N*, when the direction of the curve suddenly changes. On examining the various products under the microscope, they were all found to consist essentially of small, roughly spherical, translucent globules, faintly yellow by transmitted light but bluish-white by reflected light; some of the globules were more opaque than others and had an appearance which suggested the formation of a very fine film of minute crystals on the surface. In addition, the powder from experiment 1 contained some octahedral crystals, evidently antimonious oxide, whilst that from experiment 6 contained a number of crystals having the form of $Sb_4O_5Cl_2$. Other conditions being constant, the lower the temperature at which the reaction is carried out the

more flocculent is the condition in which the amorphous substance is precipitated and the larger will be the crop of needles ultimately obtained. A large change in the chlorine concentration of the solution following on dilution appears to favour a smaller proportion of needles in the product. The fact that only a very few needles were obtained from the hot solution where the amorphous substance was deposited in a dense form, coupled with the increased yield the more flocculent the character of the original precipitate, suggests that the needles are formed as a consequence of some change in which the flocculent substance is involved.

Although it was found impossible to prepare the needle-shaped crystals quite free from a certain amount of colloidal matter, it was found that in those preparations most free from contamination the ratio of antimony to chlorine was approximately 4 : 1; this suggested that the needles might have a composition such as $Sb_8O_{11}Cl_2$, or more probably a hydrate of this compound, seeing that the determinations both of antimony and of chlorine gave results lower than those required by the above formula. Water was evolved on heating the crystals in a dry tube, but only a small loss of weight occurred on drying at 105°; in all probability the water is present as water of constitution and not as water of crystallisation. From the loss of weight which ensues on heating the crystals in a crucible with a very small flame, coupled with the proportions in which antimony and chlorine exist in the substance, it is probable that the needles consist of $Sb_4O_3(OH)_5Cl$ or $Sb_8O_{11}Cl_2,5H_2O$. In further support of this view, attention may be directed to Fig. 2, in which the points *A* and *B* represent the compositions of $Sb_4O_3(OH)_5Cl$ and of the dried amorphous precipitate free from admixed crystals, respectively; it will be observed that the points *C* and *D*, which indicate the compositions of two of the mixtures of crystals and amorphous substance, practically fall on the line joining *A* and *B*, as should be the case if they are mixtures of $Sb_4O_3(OH)_5Cl$ and the amorphous substance. In a similar way, mixtures which contained needles, $Sb_4O_5Cl_2$, and only traces of amorphous substance gave analytical results in accordance with what would be required for mixtures of $Sb_4O_5Cl_2$ and $Sb_4O_3(OH)_5Cl$.

FIG. 2.



The above results, involving the formation of metastable colloidal and crystalline phases prior to the production of $Sb_4O_5Cl_2$, suggested that the reaction between antimonious chloride and water in more concentrated mixtures might follow a similar course. It has been mentioned that the precipitate first obtained in such circumstances is of an amorphous character and of variable composition, which suggests that it may be an adsorption product. With a view to the further investigation of the reaction, some of the concentrated solution of antimonious chloride was mixed with a little water on a microscope slide and the mixture was carefully examined from time to time. Nothing could be seen at first but an amorphous precipitate, but after a day faint dark lines appeared which eventually developed into exceedingly fine needles, and ultimately the whole of the amorphous substance was transformed into the crystalline product. Further, the mixtures in several flasks where the concentration of the liquid indicated that the stable solid phase must be SbOCl were examined before equilibrium had been established, and the solid in these mixtures was found to contain bundles of the fine needles mentioned above, although to the naked eye it appeared amorphous. It appears probable, therefore, that the amorphous precipitate first obtained on diluting concentrated solutions of antimonious chloride with water undergoes transformation into fine, needle-shaped crystals and these in their turn are converted into SbOCl. The formation of small amounts of a similar crystalline product was also observed in some of the earlier experiments to locate the transition point of $Sb_4O_5Cl_2$ and SbOCl before the crystals of the former substance made their appearance. It was impossible to make an analysis of the crystalline deposit because of the small amount of substance available and the difficulty of obtaining it uncontaminated by other products, but it is probably an oxychloride intermediate between $Sb_4O_5Cl_2$ and SbOCl, and transformable into one or other of these substances according to the concentration of the surrounding solution.

Discussion of Results.

The various results which have been described seem to be explained most satisfactorily on the following hypothesis. The addition of a sufficient amount of water to antimonious chloride brings about the complete hydrolysis of that compound, with the formation of hydrochloric acid and a highly-hydrated form of antimonious oxide, which forms a bulky, white precipitate. The precipitate tends to adsorb hydrochloric acid from the surrounding liquid, the amount of acid adsorbed and the composition of the adsorption product depending on the concentration of the solution.

The adsorption product then tends to change into an oxychloride of antimony as a result of interaction between the adsorbed acid and the adsorbent; the oxychloride so formed, however, may not be able to exist in stable equilibrium with the solution, but may in its turn suffer slow conversion into a crystalline product of different composition; probably the adsorption product changes first into that oxychloride the composition of which most nearly approximates to its own. One of these metastable substances is Cooke's oxychloride to which the formula $Sb_4O_3(OH)_5Cl$ has been assigned, whilst the other is the compound deposited in the form of fine needles from the more concentrated mixtures; as the latter can apparently suffer change into either SbOCl or $Sb_4O_5Cl_2$, according to the conditions, it would appear to have a composition intermediate between those of the substances mentioned, and the formula $Sb_4O_3(OH)_3Cl_3$ is suggested as suitable for this substance. A compound of the formula mentioned would contain 70·0 per cent. of antimony and 15·5 per cent. of chlorine; these figures agree closely with some of those obtained from the analysis of the precipitate produced by moderately diluting a concentrated solution of antimonious chloride. The process of conversion of these metastable compounds into the stable ones varies according to the nature of the final product; thus, the conversion of $Sb_4O_3(OH)_3Cl_3$ into SbOCl and $Sb_4O_5Cl_2$, respectively, will take place in accordance with the following equations:

$$Sb_4O_3(OH)_3Cl_3 + HCl = 4SbOCl + 2H_2O.$$
$$Sb_4O_3(OH)_3Cl_3 = Sb_4O_5Cl_2 + H_2O + HCl.$$

In the second reaction the solid simply gives up acid to the solution until the necessary equilibrium is established, but in the first it is necessary for interaction between the solid and the solution to occur; this difference in the nature of the process probably accounts for the more rapid attainment of equilibrium when the stable solid phase is $Sb_4O_5Cl_2$ than when it is SbOCl. In a similar manner, when a smaller proportion of hydrochloric acid is contained in the adsorption product, the latter suffers change into Cooke's oxychloride, and subsequently, according to the concentration, into $Sb_4O_5Cl_2$ or antimonious oxide. The non-production of any appreciable quantity of Cooke's oxychloride from boiling solutions is probably due to dehydration of the amorphous adsorption product at the higher temperature, which makes the separation of a crystalline hydrated oxychloride impossible. It has been mentioned that the dehydrated adsorption product was, in the most concentrated solution investigated, mixed with crystals of $Sb_4O_5Cl_2$, and from this it would appear that the latter oxychloride

may, under certain conditions, be formed directly from the adsorption compound.

The above hypothesis, involving complete hydrolysis of antimonious chloride as the first stage of the reaction, appears to agree better with the various observations made by the authors than does the more commonly accepted view which involves progressive hydrolysis; the formation and behaviour of the metastable substances cannot be readily accounted for in terms of the latter hypothesis.

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XIX.—p-*Bromophenyltrimethylammonium Perhalides.*

By THOMAS HAROLD READE.

THE study of the phenyltrimethylammonium perhalides investigated by McCombie and Reade (T., 1923, **123**, 141) has been extended to the *p*-bromophenyltrimethylammonium series in this communication and to the *p*-iodophenyltrimethylammonium series (Reade and Sim, following paper). The result of degrading perhalides by acetone has yielded analogous quaternary ammonium salts in all three series. For example :

	Perhalide (empirical formula).		Product isolated.		Part removed by acetone.
(*a*)*	$QmCl_2I$	→	QmCl	+	ICl
(*b*)	$QmCl_2Br$	→	QmBr	+	Cl_2
(*c*)	QmClBrI	→	QmBr	+	ICl
(*d*)*	$QmBr_2I$	→	QmBr	+	IBr

where Qm = $NPhMe_3$ or, when marked with asterisk, $(p)C_6H_4Br{\cdot}NMe_3$ or $(p)C_6H_4I{\cdot}NMe_3$.

In view of the marked electronegative nature of chlorine, reactions (*b*) and (*c*) are noteworthy, since the quaternary salt isolated was the bromide, not the chloride.

The table on p. 149 summarises the results of submitting *p*-bromophenyltrimethylammonium halides and perhalides to the further action of the halogens.

The points of difference between this series and the unsubstituted phenyltrimethylammonium perhalides were :

(1) That $QmBrI_2$ yielded QmBr in the *p*-bromo-series when treated with acetone, whereas its analogue in the unsubstituted phenyl series was not attacked.

(2) That well-defined, double perhalides have been obtained in several reactions; for example, ($QmCl_2I$ + QmClBrI) resulted from

TABLE I.

Formation.	Empirical formula.	Product from acetone.	Structural formula.	Product of chlorination.	Product of bromination.	Product of iodination.	ICl or IBr.
p-$C_6H_4Br{\cdot}NMe_2+CH_3I$	QmI	—	QmI	QmCl,ICl_3	QmBr,IBr	QmI_3	QmBr,I_2
$QmBr_3$+acetone	QmBr	—	QmBr	QmBr,Cl_2	$QmBr_3$	QmBr,I_2	QmBr,ICl QmBr,IBr
QmCl,ICl+acetone	QmCl	—	QmCl	Unchanged	$QmBr_3$ (80%)	QmI_3 (65%) QmI_5 and ICl	QmCl,ICl QmBr,ICl
QmCl+IBr QmBr+ICl	QmClBrI	QmBr	QmBr,ICl	$QmCl,ICl_3$	QmBr,IBr and QmBr,ICl	[QmBr,I_2 QmBr,ICl]	—
QmI+Br_2 QmBr+IBr	$QmBr_2I$	QmBr	QmBr,IBr	$QmCl,ICl_3$	Unchanged	[QmBr,I_2 QmBr,IBr]	—
QmI+Cl excess	$QmCl_4I$	QmCl	QmCl,ICl_3	Unchanged	"	QmCl,ICl	—
QmCl,ICl_3+ethyl malonate	$QmCl_2I$	QmCl	QmCl,ICl	$QmCl,ICl_3$	[QmBr,ICl QmCl,ICl]	Unchanged+iodine-containing products	—
$QmBr_3$+Cl excess QmBr+Cl excess	$QmCl_2Br$	QmBr	QmBr,Cl_2	Unchanged	Unchanged	QmBr,ICl from 1 atomic proportion of iodine	—
Qm·SO_4Me+HBr+Br_2 QmBr+Br_2	$QmBr_3$	QmBr	$QmBr_3$	QmBr,Cl_2	—	QmBr,IBr	—
QmBr+I_2	$QmBrI_2$	QmBr pure but small yield	QmBr,I_2	QmCl,ICl_3	QmBr,IBr	Dark brown product which with acetic acid gave QmBr,I_2 and QmI_3	—
QmI+I_2	QmI_3	Unchanged	QmI_3	QmCl,ICl_3	QmBr,IBr	QmI_5 and QmI_3	—

Qm denotes *p*-bromophenyltrimethylammonium.

the action of bromine on $QmCl_2I$, gave identical analytical figures after crystallisation from ethyl alcohol or acetic acid, and yielded a mixture of QmCl and QmBr on degradation by acetone.

No exception to the statement that chlorine replaces the *N*-halogen in iodides and periodides, that it replaces *N*-bromine only when iodine is also present, and that it replaces added halogens in perbromides (giving $QmBr,Cl_2$) has been encountered. But bromine and iodine replace *N*-chlorine to an appreciable extent, and iodine replaces *N*-bromine in one instance. Consequently, the generalisations for the replacement of halogen atoms in the phenyltrimethylammonium perhalides, although useful as a guide, are not rigidly applicable to this series of perhalides.

EXPERIMENTAL.

Identification.—Owing to the rapidity with which decomposition takes place at the temperature of fusion, the melting point is of little value as a criterion of purity of these perhalides.

Analysis.—Mixed halogens have been estimated by Carius's method, and also by a method described by Reade and Sim (following paper) whereby the ionisable halogens only are estimated, the *p*-bromine atom not being attacked.

Degradation.—(*a*) Ethyl malonate and (*b*) acetone have been used exactly as described by McCombie and Reade (*loc. cit.*).

p-*Bromophenyltrimethylammonium Methyl Sulphate*, $C_6H_4Br{\cdot}NMe_3{\cdot}SO_4Me$.

—*p*-Bromodimethylaniline (100 grams), diluted with 500 c.c. of benzene, was heated for five hours under reflux with 49 c.c. of methyl sulphate. After cooling, the product, part crystalline and part oil, was separated, heated under reflux with 200 c.c. of dry acetone, and cooled. The solid thus obtained was twice recrystallised from alcohol and ether, yielding white crystals, m. p. 208° with decomposition, which were readily soluble in methyl or ethyl alcohol and sparingly soluble in benzene, xylene, chloroform, or ether (Found : $SO_4 = 29{\cdot}85$; C = 36·3; H = 4·8. $C_6H_4Br{\cdot}NMe_3{\cdot}SO_4Me$ requires $SO_4 = 29{\cdot}45$; C = 36·8; H = 4·9 per cent.).

When treated with bromine in hydrobromic acid solution, it gave an orange perbromide, $C_6H_4Br{\cdot}NMe_3Br_3$.

p-*Bromophenyltrimethylammonium perbromide*, $C_6H_4Br{\cdot}NMe_3Br_3$, was prepared by heating 24 grams of *p*-bromodimethylaniline, 8 grams of methyl sulphate, and 30 c.c. of pure methyl alcohol under reflux for six hours. The methyl alcohol was then distilled, the residue digested with water, and 32 grams of potassium bromide, 23 grams of bromine, and 10 c.c. of glacial acetic acid were added, whereby 34 grams of the perbromide were precipitated, which

crystallised from acetic acid in orange-red leaflets, m. p. 175° with decomposition (Found : Br = 70·4. $C_6H_4Br{\cdot}NMe_3Br_3$ requires Br = 70·3 per cent.).

This perbromide yielded the bromide $C_6H_4Br{\cdot}NMe_3Br$ when warmed with acetone.

Iodine in acetic acid gave $C_6H_4Br{\cdot}NMe_3Br,IBr$ (Found : Br = 29·8; I = 28·8. Calc., Br = 31·8; I = 25·3 per cent.).

Chlorine in acetic acid gave $C_6H_4Br{\cdot}NMe_3Br,Cl_2$, pale lemon-yellow plates melting at 158° with decomposition after crystallisation from acetic acid.

p-*Bromophenyltrimethylammonium bromide*, $C_6H_4Br{\cdot}NMe_3Br$, is formed when the corresponding iodide is shaken with excess of silver bromide. It is best prepared, however, by shaking the perbromide $C_6H_4Br{\cdot}NMeBr_3$ with five times its weight of dry acetone; the bromide is precipitated after a few minutes, the yield being 85 per cent. of the theoretical. It forms white crystals from alcohol, which darken at 200° and melt at 210°. The compound is insoluble in chloroform or acetone, easily soluble in acetic acid or alcohol, and very easily soluble in hot water (Found : C = 36·6; H = 4·4; Br = 54·2. $C_6H_4Br{\cdot}NMe_3Br$ requires C = 36·6; H = 4·4; Br = 54·24 per cent.).

The action of halogens in acetic acid on this bromide was as follows: chlorine gave the bromodichloride, $C_6H_4Br{\cdot}NMe_3Br,Cl_2$, m. p. 158°; bromine gave the perbromide, $C_6H_4Br{\cdot}NMe_3Br_3$, m. p. 172°; and iodine gave the bromodi-iodide, $C_6H_4Br{\cdot}NMe_3BrI_2$, m. p. 172°.

Iodine monochloride gave the bromo-iodochloride,

$$C_6H_4Br{\cdot}NMe_3Br,ICl,$$

m. p. 181°, whilst iodine monobromide gave the bromo-iodobromide, $C_6H_4Br{\cdot}NMe_3Br,IBr$, melting at 185° with decomposition.

Action of Halogens on p-*Bromophenyltrimethylammonium Iodide.*—Chlorine in glacial acetic acid at 60° gave *p*-bromophenyltrimethylammonium chloride iodotrichloride, $C_6H_4Br{\cdot}NMeCl,ICl_3$, m. p. 187°. Bromine under similar conditions gave *p*-bromophenyltrimethylammonium bromo-iodobromide, orange plates, m. p. 185°.

Iodine (1 mol.) in alcohol, or in acetic acid, gave the tri-iodide $C_6H_4Br{\cdot}NMe_3,I_3$, coppery plates, m. p. 172°; whilst iodine (2 mols.) gave brownish-black, shining leaflets which were recrystallisable from acetic acid without change, but gave the tri-iodide only when crystallised from alcohol (the thiosulphate titration value for the brownish-black leaflets was 1 per cent. below that required for the aggregate $C_6H_4Br{\cdot}NMe_3I,I_4 + C_6H_4Br{\cdot}NMe_3I,I_2$).

p-*Bromophenyltrimethylammonium Tri-iodide*, $C_6H_4Br{\cdot}NMe_3I_3$.—Equimolecular quantities of iodine and $C_6H_4Br{\cdot}NMe_3I$ were mixed in methylated spirit at 70°, and the solution was allowed to cool,

when brown, coppery plates, melting with decomposition at 172°, crystallised. The yield was 80 per cent. of the theoretical (Found: I′ = 63·9. $C_6H_4Br{\cdot}NMe_3I_3$ requires I′ = 63·9 per cent.).

The crystals are very easily soluble in acetone, and easily soluble in hot alcohol or in hot acetic acid, from which they crystallise on cooling.

Action of Halogens.—Chlorine in acetic acid gave

$$C_6H_4Br{\cdot}NMe_3Cl,ICl_3$$

(Found: 0·1862 gave by the Carius method 0·3831 of silver halides, which gave 0·3369 of AgCl. Calc., 0·3840 of silver halides, giving 0·3320 of AgCl).

Bromine (2 mols.) in acetic acid gave $C_6H_4Br{\cdot}NMe_3Br,IBr$, orange plates, m. p. 185°.

p-*Bromophenyltrimethylammonium Chloride Iodotrichloride,*

$$C_6H_4Br{\cdot}NMe_3Cl,ICl_3.$$

—This substance can be prepared by the action of chlorine on an acetic acid solution of any of the following perhalides:

$$C_6H_4Br{\cdot}NMe_3Br,ICl,$$

$C_6H_4Br{\cdot}NMe_3Br,IBr$, $C_6H_4Br{\cdot}NMe_3Cl,ICl$, $C_6H_4Br{\cdot}NMe_3Br,I_2$, $C_6H_4Br{\cdot}NMe_3I_3$. It was prepared by the chlorination of 16 grams of *p*-bromophenyltrimethylammonium iodide in 1 litre of hot glacial acetic acid, the yield being 17 grams. It crystallised from acetic acid in canary-yellow needles; m. p. 186—189° with decomposition (Found: 0·3046 gave 0·6199 of mixed silver halides, which yielded after chlorination the ratio silver halides/AgCl = 1·15. $C_6H_4Br{\cdot}NMe_3Cl,ICl_3$ requires 0·6270 of mixed halides and the ratio 1·16).

Degradation by dry acetone at 25° yielded the chloride,

$$C_6H_4Br{\cdot}NMe_3Cl$$

(Found: Cl′ = 14·1, 13·9. Calc., Cl′ = 14·16 per cent.).

Degradation by ethyl malonate at 60° in a vacuum gave the crude dichloroiodide in 90 per cent. yield (Found: 0·1530 gave 0·2702 of silver halides, which yielded after chlorination the ratio silver halides/AgCl = 1·22. $C_6H_4Br{\cdot}NMe_3Cl,ICl$ requires 0·2635 of silver halides and the ratio 1·237).

Attempts to purify the crude product by crystallisation from ethyl alcohol proved abortive, a series of perhalides being obtained which contained less chlorine the longer the period of treatment.

Very rapid crystallisation from alcohol gave yellow crystals approximating in composition to the formula $C_6H_4Br{\cdot}NMe_3Cl,ICl$ (Found: 0·2333 gave 0·3875 of mixed silver halides, which yielded after chlorination the ratio mixed halides/AgCl = 1·27. Calc., 0·4010 of mixed halides and the ratio 1·24).

The substance was heated with alcohol for ten minutes; red

needles were obtained on cooling, the yield being 45 per cent. (Found : C = 23·5; H = 2·8; 0·1000 gave 0·1626, 0·1639 of mixed silver halides, which after chlorination gave the ratio mixed halides/AgCl = 1·34. $C_6H_4Br{\cdot}NMe_3Cl,ICl + C_6H_4Br{\cdot}NMe_3Cl,I_2$ requires C = 23·5; H = 2·83 per cent.; mixed halides 0·1645 and ratio 1·32).

If heating in alcohol was continued for two hours, coppery plates of $C_6H_4Br{\cdot}NMe_3I_3$ crystallised on cooling, whilst the mother-liquor, on addition of ether, yielded a precipitate of $C_6H_4Br{\cdot}NMe_3Cl$, which was converted into its double salt with mercuric chloride (Found : Cl′ = 19·9. $C_6H_4Br{\cdot}NMe_3Cl,HgCl_2$ requires Cl′ = 20·4 per cent.).

Chlorine and bromine in acetic acid were without action on $C_6H_4Br{\cdot}NMe_3Cl,ICl_3$; iodine, however, gave $C_6H_4Br{\cdot}NMe_3Cl,ICl$ (Found : Cl = 18·7; I = 26·5. Calc., Cl = 17·2; I = 30·7 per cent.).

p-*Bromophenyltrimethylammonium Chloride Iodochloride*,

$C_6H_4Br{\cdot}NMe_3Cl,ICl$.

—Chlorine was passed into an acetic acid solution of *p*-bromophenyltrimethylammonium iodide at 70° until the colour of the solution was a clear claret-red; the product crystallised, on cooling, in bright yellow needles, m. p. 177° with decomposition (The m. p. of a specimen which had been kept in the light for one month was 165°). The substance is easily soluble in hot ethyl alcohol, methyl alcohol, or acetic acid (Found : 0·1000 and 0·1000 gave 0·1261 and 0·1267, respectively, of AgCl + AgI. $C_6H_4Br{\cdot}NMeCl,ICl$ requires 0·1264 of AgCl + AgI).

Degradation.—Acetone at 25° gave a red solution and precipitated $C_6H_4Br{\cdot}NMe_3Cl$ (free from iodide), which was converted into its double salt with mercuric chloride for analysis (Found : Cl′ = 20·17. $C_6H_4Br{\cdot}NMe_3Cl,HgCl_2$ requires Cl′ = 20·42 per cent.).

Action of Halogens.—Chlorine gave $C_6H_4Br{\cdot}NMe_3Cl,ICl_3$; iodine gave traces of periodides with much unchanged dichloroiodide; bromine gave a golden-yellow double perhalide,

$C_6H_4Br{\cdot}NMe_3Cl,ICl + C_6H_4Br{\cdot}NMe_3Br,ICl$,

recrystallisable from acetic acid or ethyl alcohol (Found : 0·1000 of material crystallised from acetic acid gave 0·1248 of ionisable silver halides, which after chlorination gave the ratio silver halides/AgCl = 1·261. 0·1000 of material crystallised from alcohol gave 0·1249 of silver halides, and the ratio 1·260. $C_6H_4Br{\cdot}NMe_3Cl,ICl + C_6H_4Br{\cdot}NMe_3Br,ICl$ requires 0·1250 of silver halides and the ratio 1·263).

This double perhalide gave a mixture of the quaternary chloride and bromide when treated with acetone (Found : Br′ = 19·7; Cl′ = 3·6. Calc. for $C_6H_4Br{\cdot}NMe_3Br$, Br′ = 27·1; and for $C_6H_4Br{\cdot}NMe_3Cl$, Cl′ = 13·1 per cent.).

p-*Bromophenyltrimethylammonium Chloride*, $C_6H_4Br{\cdot}NMe_3Cl$.—This substance, prepared by the action of dry acetone on

$C_6H_4Br{\cdot}NMe_3Cl,ICl$,

forms hygroscopic, white crystals, very easily soluble in water, easily soluble in hot ethyl alcohol, sparingly soluble in boiling acetone, and slightly soluble in cold acetone, benzene, or ether. It darkens at 191° and melts with decomposition at 199°. With aqueous potassium iodide, $C_6H_4Br{\cdot}NMe_3I$ is precipitated.

Action of Halogens in Acetic Acid.—Chlorine was without action. Bromine gave $C_6H_4Br{\cdot}NMe_3Br_3$ in 80 per cent. yield (Found : $Cl' = 1{\cdot}2$; $Br' = 49{\cdot}6$. Calc., $Br' = 52{\cdot}7$ per cent.).

Iodine gave chocolate-coloured crystals, green in thin layers, melting at 172°, consisting of $C_6H_4Br{\cdot}NMe_3I_3 + C_6H_4Br{\cdot}NMe_3I_5$, whilst iodine monochloride remained in the solution (Found : $I = 69$. Calc., $I = 70{\cdot}3$ per cent.).

Iodine monobromide (1 mol.) in cold acetic acid gave an immediate precipitate of $C_6H_4Br{\cdot}NMe_3Br,ICl$, melting at 177°, which on treatment with acetone yielded chiefly the bromide (Found : $Br' = 24$; $Cl' = 2$. Calc. for $C_6H_4Br{\cdot}NMe_3Br$, $Br' = 27{\cdot}1$ per cent.).

Iodine monochloride (1 mol.) gave pale yellow crystals of

$C_6H_4Br{\cdot}NMe_3Cl,ICl$

(Found : 0·0724 gave 0·1254 of ionisable silver halides. Calc., 0·1245).

p-*Bromophenyltrimethylammonium Bromide Iodobromide*,

$C_6H_4Br{\cdot}NMe_3Br,IBr$.

—Eight grams of bromine were added to 16 grams of *p*-bromophenyltrimethylammonium iodide in 1 litre of glacial acetic acid at 80°. Orange, laminated plates crystallised on cooling. These began to darken at 170° and melted with decomposition at 189°. Yield 13½ grams. The mother-liquor was used for a second preparation and yielded 20 grams [Found : Br (total) = 45·2; Br (ionisable) = 30·3; $I = 27{\cdot}7$. $C_6H_4Br{\cdot}NMe_3Br,IBr$ requires total Br = 47·7; ionisable Br = 31·9; $I = 25{\cdot}3$ per cent.].

The constitution was inferred from its yielding (*a*) the bromide $C_6H_4Br{\cdot}NMe_3Br$ when treated with acetone, and (*b*) a pink colour in dilute acetic acid solution when treated with aqueous starch solution.

Action of Halogens in Acetic Acid.—Chlorine gave yellow crystals of $C_6H_4Br{\cdot}NMe_3Cl,ICl_3$, m. p. 185°; bromine was without action; whilst iodine gave a red, double perhalide, $C_6H_4Br{\cdot}NMe_3Br,IBr + C_6H_4Br{\cdot}NMe_3Br,I_2$, m. p. 185° with decomposition, crystallisable from alcohol or acetic acid (Found : $I = 36{\cdot}8$; $Br' = 22{\cdot}3$. Calc., $I = 36{\cdot}3$; $Br' = 22{\cdot}8$ per cent.).

p-*Bromophenyltrimethylammonium bromide di-iodide*,

$C_6H_4Br{\cdot}NMe_3Br,I_2$,

was prepared by mixing hot acetic acid solutions containing equimolecular quantities of iodine and $C_6H_4Br{\cdot}NMe_3Br$. The reddish-brown crystals, after two crystallisations from acetic acid, melted at 172° with decomposition (Found : 0·1917 gave 0·2960 of mixed silver halides. $C_6H_4Br{\cdot}NMe_3Br,I_2$ requires 0·2952 of silver halides).

Its constitution was inferred from its giving (*a*) in dilute acetic acid solution an intense blue colour with starch, and (*b*) 10 per cent. of the bromide $C_6H_4Br{\cdot}NMe_3Br$ after twenty-four hours' treatment with acetone at 18°.

Action of Halogens in Acetic Acid.—Chlorine gave yellow needles of $C_6H_4Br{\cdot}NMe_3Cl,ICl_3$, m. p. 186°; bromine gave orange plates of $C_6H_4Br{\cdot}NMe_3Br,IBr$, m. p. 189°; iodine gave a mixture of the tri-iodide, $C_6H_4Br{\cdot}NMe_3I_3$, and unchanged bromide di-iodide.

p-*Bromophenyltrimethylammonium Bromide Iodochloride*,

$C_6H_4Br{\cdot}NMe_3Br,ICl$.

—Equimolecular quantities of iodine monochloride and

$C_6H_4Br{\cdot}NMe_3Br$

were dissolved separately in hot acetic acid and the solutions mixed. Sandy, yellow crystals, which darken at 165° and melt at 178—179° with decomposition, separated on cooling (Found : 0·2026 gave 0·3344 of mixed silver halides, which after chlorination gave the ratio total silver halides/AgCl = 1·30. $C_6H_4Br{\cdot}NMe_3Br,ICl$ requires 0·3340 of mixed halides and the ratio 1·31). It was also formed by adding iodine monobromide to $C_6H_4Br{\cdot}NMe_3Cl$ in acetic acid.

Degradation by acetone yielded the bromide, with traces only of the chloride (Found : for the crude, dried product, Br′ = 24·2; Cl′ = 1·4. Calc. for $C_6H_4Br{\cdot}NMe_3Br$, Br′ = 27·1 per cent.).

Action of Halogens in Acetic Acid.—Chlorine gave

$C_6H_4Br{\cdot}NMe_3Cl,ICl_3$,

m. p. 186°. Bromine gave a mixture of $C_6H_4Br{\cdot}NMe_3Br,IBr$ and $C_6H_4Br{\cdot}NMe_3Br,ICl$ (Found : 0·1477 gave 0·1810 of ionisable mixed silver halides, which after chlorination yielded the ratio mixed silver halides/AgCl = 1·39. $C_6H_4Br{\cdot}NMe_3Br,IBr$ requires 0·1796 of silver halides and the ratio 1·42. $C_6H_4Br{\cdot}NMe_3Br,ICl$ requires 0·1828 of silver halides and the ratio 1·32).

Iodine gave red needles, m. p. 182°, of a double perhalide, crystallisable from alcohol or acetic acid (Found : 0·1000 of material crystallised from acetic acid gave 0·1216 of ionisable silver halides, which yielded after chlorination the ratio silver halides/AgCl = 1·38. Found : in material crystallised from alcohol, 0·1000 and 0·1000 gave 0·1223 and 0·1212 of silver halides and the ratio 1·38 and 1·39,

respectively. $C_6H_4Br{\cdot}NMe_3Br,I_2 + C_6H_4Br{\cdot}NMe_3Br,ICl$ requires 0·1219 of silver halides and the ratio 1·42).

Degradation by acetone gave $C_6H_4Br{\cdot}NMe_3Br$.

p-Bromophenyltrimethylammonium bromide dichloride,

$C_6H_4Br{\cdot}NMe_3Br,Cl_2$,

was precipitated when *p*-bromophenyltrimethylammonium bromide in acetic acid at 60° was added to acetic acid saturated with chlorine at 18°. Recrystallised from acetic acid heated to 75° only, it formed greenish-yellow crystals which lose chlorine readily and melt at 158° with rapid decomposition (Found : Cl = 17·6; Br = 46·1. $C_6H_4Br{\cdot}NMe_3Br,Cl_2$ requires Cl = 19·4; Br = 43·7 per cent.).

Degradation by acetone gave $C_6H_4Br{\cdot}NMe_3Br$ (Found : Br′ = 27·4. Calc., Br′ = 27·1 per cent.).

Action of Halogens in Acetic Acid.—Chlorine or bromine was without action. Iodine (½ mol.), however, gave $C_6H_4Br{\cdot}NMe_3Br,ICl$, m. p. 178°, which gave $C_6H_4Br{\cdot}NMe_3Br$ when degraded by acetone.

Summary.

The reactions between *p*-bromophenyltrimethylammonium halides and molecular halogen, yielding perhalides, are described.

The reaction, Perhalide + acetone ⟶ quaternary ammonium salt + halogenated acetone has been utilised to classify these perhalides, and has given results analogous to those obtained by McCombie and Reade (*loc. cit.*) for phenyltrimethylammonium perhalides, thus affording support to the view that this reaction is of service in determining the constitution of perhalides.

The results of treating *p*-bromophenyltrimethylammonium perhalides with molecular halogen are included in Table I, and indicate that the mobility of the halogen atoms in perhalides is in many cases greater than that which would be inferred from the generalisations given by McCombie and Reade (*loc. cit.*). The following statement, however, is applicable to both series; chlorine invariably replaces the *N*-halogen in the quaternary ammonium iodide, or in periodides. It replaces *N*-bromine only when iodine is also present, but replaces "added bromine" in $QmBr,Br_2$, giving $QmBr,Cl_2$, where *N*-halogen and "added bromine" are used in the sense defined by McCombie and Reade.

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XX.—p-*Iodophenyltrimethylammonium Perhalides.*

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WHEN perhalides of the phenyltrimethylammonium series were under investigation, it seemed of interest to inquire whether perhalides could be obtained in the *p*-iodophenyltrimethylammonium series, or whether the *p*-iodine atom would enter into reaction with chlorine, giving iodochlorides similar in properties to those given by iodobenzene, iodophenols, iodo-acids, etc. It seemed probable that the investigation might lead to the production of either (1) perhalides similar to those of the phenyltrimethylammonium series, (2) *p*-iodochlorides, or (3) substances which were both *p*-iodochlorides and perhalides.* Moreover, there appeared to be a possibility that the residual affinities of the ionic iodine and the *p*-iodine atoms might mutually saturate each other, so that additive compounds with the halogens would not be obtainable.

By passing a very rapid stream of chlorine into a dilute acetic acid solution of the quaternary ammonium iodide, it is possible, on cooling, to isolate yellow crystals which approximate closely to the formula $C_6H_4I{\cdot}NMe_3Cl_4I$. This product can be degraded with ethyl malonate, yielding the dichloroiodide $C_6H_4I{\cdot}NMe_3Cl_2I$, but this can be isolated in a state of purity only when a solvent of low boiling point, for example, methyl alcohol, is employed as crystallising medium. The pure dichloroiodide on treatment with dry acetone yielded the quaternary ammonium chloride.

If the dichloroiodide was treated with hot glacial acetic acid, a double perhalide, of a darker shade of yellow, crystallised out, the formula of which approximated to $C_6H_4I{\cdot}NMe_3Cl_2I + C_6H_4I{\cdot}NMe_3ClI_2$. This yellowish-brown product, when treated with acetone, yielded the quaternary ammonium iodide, contaminated with 3 per cent. of the chloride. Wright's results are probably to be attributed to changes taking place in the dichloroiodide during crystallisation from acetic acid.

This communication also describes a new method of preparation

* An investigation on these lines by Wright and McCombie gave results which may be summarised as follows: Iodo-chlorides were not obtained. Perhalides of the forms $C_6H_4I{\cdot}NMe_3Cl_2I$ and $C_6H_4I{\cdot}NMe_3Br_2I$ were isolated. Of these, the latter gave the bromide when treated with acetone, and its behaviour was strictly analogous to that met with in the phenyltrimethylammonium and the *p*-bromophenyltrimethylammonium series. The former, the dichloroiodide, gave the iodide, not the chloride, when treated with acetone. It was also found that the tetrachloroiodide was not isolated in this series. Inasmuch as the original collaborators discontinued this work, these two points have been re-investigated.

of *p*-iododimethylaniline, the formation of *p*-iodophenyltrimethylammonium tri-iodide, and a rapid and convenient method of estimating the ionisable mixed halogens in perhalides.*

EXPERIMENTAL.

p-Iododimethylaniline, $C_6H_4I{\cdot}NMe_2$.—To a solution of 30 c.c. of dimethylaniline in 100 c.c. of glacial acetic acid at 18°, 30 grams of iodine and 3 grams of iodic acid were gradually added, with constant shaking and cooling, during thirty minutes. The settled solution was decanted from the small quantity of unchanged iodine, made strongly alkaline with sodium hydroxide, and stirred until the solid product became granular; this was collected after twelve hours and recrystallised from alcohol, 28 grams of white crystals, m. p. 78·5°, identical with those prepared by the usual method of iodination in carbon disulphide, being obtained.

p-Iodophenyltrimethylammonium Iodide, $C_6H_4I{\cdot}NMe_3I$.—A mixture of 6·5 c.c. of methyl iodide, 20 c.c. of methyl alcohol, and 20·4 grams of *p*-iododimethylaniline was gently heated under reflux for six hours. The white product after recrystallisation from methyl alcohol melted at 190·5°, the yield being 23 grams. Ethyl alcohol may be substituted for methyl alcohol [Found : I (total) = 64·7; I (ionisable) = 32·5. $C_6H_4I{\cdot}NMe_3I$ requires I (total) = 65·3; I (ionisable) = 32·65 per cent.]. This substance is readily soluble in hot alcohol or methyl alcohol and sparingly soluble in water, ether, or acetone. When treated with chlorine in acetic acid, it yields yellow crystals of $C_6H_4I{\cdot}NMe_3Cl,ICl_3$, whilst iodine (1 mol.) in alcohol gave the tri-iodide, $C_6H_4I{\cdot}NMe_3I_3$.

p-Iodophenyltrimethylammonium Chloride Iodotrichloride, $C_6H_4I{\cdot}NMe_3Cl,ICl_3$.—A rapid stream of chlorine was led into 10 grams of $C_6H_4I{\cdot}NMe_3I$ in 150 c.c. of glacial acetic acid at 60°, and was continued while the solution was cooled to 20°. Bright yellow needles crystallised out, m. p. 187° with decomposition. Further recrystallisation from acetic acid did not affect the melting point. The crystals lose chlorine somewhat readily when left in a desiccator (Found : Cl′ = 24·4; I′ = 24·9. $C_6H_4I{\cdot}NMe_3Cl_4I$ requires Cl′ = 26·9; I′ = 24·05 per cent.). Its constitution was determined by treating the substance with ethyl malonate at 30—40°, under reduced pressure; the dichloro-iodide,

$$C_6H_4I{\cdot}NMe_3Cl_2I,$$

obtained, on treatment with acetone, gave *p*-iodophenyltrimethylammonium chloride.

* One of the collaborators (S. A. S.) has discontinued this investigation, so the work is submitted for publication in its present state.

p-*Iodophenyltrimethylammonium Chloride Iodochloride*, $C_6H_4I{\cdot}NMe_3Cl,ICl$.—A solution of 4 grams of the tetrachloroiodide in 35 grams of ethyl malonate was heated to 40° and placed in a desiccator, which was then evacuated, the process being repeated until no more gas was evolved. The golden-yellow, crystalline compound was washed with ether and recrystallised from methyl alcohol. It then melted at 184° with decomposition. The yield was 3 grams (Found: $Cl' = 15{\cdot}43$; $I' = 28{\cdot}9$. $C_6H_4I{\cdot}NMe_3Cl,ICl$ requires $Cl' = 15{\cdot}42$; $I' = 27{\cdot}6$ per cent.). When this compound was shaken with dry acetone, the quaternary ammonium chloride was precipitated (Found: $Cl' = 11{\cdot}90$. Calc., $Cl' = 11{\cdot}92$ per cent.). Thus the dichloroiodide is the iodine monochloride compound of the quaternary ammonium chloride.

Influence of Heat on the Iodochloride.—Whenever this compound in solution was submitted to a high temperature, for example, in boiling glacial acetic acid, or in ethyl malonate at temperatures above 40°, the product which crystallised on cooling was brown, and contained less chlorine and relatively more iodine than the unchanged dichloroiodide (Found: $Cl = 11{\cdot}90$; $I = 37{\cdot}8$. Calc. for $C_6H_4I{\cdot}NMe_3Cl,ICl$, $Cl = 15{\cdot}56$; $I = 27{\cdot}8$. $C_6H_4I{\cdot}NMe_3Cl,ICl + C_6H_4I{\cdot}NMe_3ClI_2$ requires $Cl = 10{\cdot}60$; $I = 38{\cdot}0$ per cent.). Since the di-iodochloride has not yet been isolated, the double perhalide formula is put forward tentatively; but it is supported by the fact that this substance yielded chiefly the quaternary ammonium iodide (97 per cent. with about 3 per cent. of the quaternary ammonium chloride) when treated with acetone (Found: $I' = 31{\cdot}0$; $Cl' = 1{\cdot}1$. Calc. for $C_6H_4I{\cdot}NMe_3I$, $I' = 32{\cdot}8$ per cent.).

p-*Iodophenyltrimethylammonium Tri-iodide*, $C_6H_4I{\cdot}NMe_3I_3$.—Equimolecular quantities of iodine and *p*-iodophenyltrimethylammonium iodide in alcohol were heated together under reflux. On cooling, brown leaflets of the tri-iodide crystallised out (Found: $I' = 59{\cdot}4$. $C_6H_4I{\cdot}NMe_3I_3$ requires $I' = 59{\cdot}3$ per cent.). This substance melts with decomposition at 189° and is best recrystallised from alcohol.

Estimation of Ionisable Halogens in Perhalides.

Notwithstanding the fact that perhalides are somewhat unstable substances, no rapid and trustworthy methods of analysis have hitherto been described. Volumetric methods involve in their calculation a knowledge of what halogens are present, whether chlorine, bromine, or iodine, and estimation by Carius's method is slow. The need for a more rapid method than the latter, and especially for one which does not take account of the *p*-halogen

of *p*-iododimethylaniline, the formation of *p*-iodophenyltrimethylammonium tri-iodide, and a rapid and convenient method of estimating the ionisable mixed halogens in perhalides.*

EXPERIMENTAL.

p-*Iododimethylaniline*, $C_6H_4I{\cdot}NMe_2$.—To a solution of 30 c.c. of dimethylaniline in 100 c.c. of glacial acetic acid at 18°, 30 grams of iodine and 3 grams of iodic acid were gradually added, with constant shaking and cooling, during thirty minutes. The settled solution was decanted from the small quantity of unchanged iodine, made strongly alkaline with sodium hydroxide, and stirred until the solid product became granular; this was collected after twelve hours and recrystallised from alcohol, 28 grams of white crystals, m. p. 78·5°, identical with those prepared by the usual method of iodination in carbon disulphide, being obtained.

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Estimation of Ionisable Halogens in Perhalides.

Notwithstanding the fact that perhalides are somewhat unstable substances, no rapid and trustworthy methods of analysis have hitherto been described. Volumetric methods involve in their calculation a knowledge of what halogens are present, whether chlorine, bromine, or iodine, and estimation by Carius's method is slow. The need for a more rapid method than the latter, and especially for one which does not take account of the *p*-halogen

atom in the phenyl group in this series, resulted in the following procedure being adopted.

The accurately weighed perhalide was added to an excess of a hot 4*N*-solution of sodium carbonate, to which had been added a weight of sodium sulphite equal to that of the perhalide. After dissolution, the liquid was faintly acidified with dilute nitric acid, aqueous silver nitrate (containing $AgNO_3 = 2\frac{1}{2}$ times the weight of the perhalide) added, and the solution boiled to expel sulphur dioxide and diluted (to prevent precipitation of silver sulphate). The precipitate, collected in a Gooch crucible, was dried and weighed. The silver halide was then heated at 200° in a stream of chlorine until entirely converted into silver chloride.

The above method has proved convenient and fairly accurate in the case of *p*-bromo- and *p*-iodo-phenyltrimethylammonium perhalides. The first two estimations may be cited as representative examples of the degree of accuracy obtainable, although many of the later estimations gave more concordant results.

A synthetic specimen of $C_6H_4Br{\cdot}NMe_3Cl,ICl$ of known purity gave the following figures: 0·1000 and 0·1000 gave 0·1261 and 0·1267, respectively, of mixed AgCl and AgI. Calc., 0·1264.

A series of blank estimations showed that the para-halogen atom was not attacked by this method of estimation.

Grateful acknowledgment is made of a Robbie Research Scholarship awarded to one of us (S. A. S.).

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UNIVERSITY OF ABERDEEN. [*Received, August 20th*, 1923.]

XXI.—*The Dependence of Polarisation-overvoltage on Hydroxyl- and Hydrogen-ion Concentration. Part I. Polarisation-overvoltage of an Antimony Cathode in Aqueous Alkaline Solution.*

By HENRY JULIUS SALOMON SAND and EDWARD JOSEPH WEEKS.

IN a previous communication (T., 1923, **123**, 456), it was shown that the polarisation-overvoltage of an antimony cathode is lowered by high concentrations of sulphuric acid or of sodium hydroxide, and it was pointed out that a close relation would probably be found to exist between the overvoltage and the concentration of hydrogen- or of hydroxyl-ions. In the experiments now to be recorded, the dependence of the polarisation-overvoltage of an

antimony cathode on hydroxyl-ion concentration has been further studied.

Experimental.

The following electrolytes have been employed: sodium hydroxide, sodium sulphide, ammonium hydroxide, sodium carbonate, sodium phosphate, sodium bicarbonate, sodium sulphate, potassium chloride, and also mixtures of sodium hydroxide and potassium chloride.

It was shown in the previous paper that when the commutator method of measuring overvoltage is employed, definite values are reached in a given electrolyte of definite temperature when a certain "critical" current density is exceeded and the speed of the commutator is sufficiently great. These results have been confirmed. We propose in future to refer, where necessary, to overvoltages determined by the commutator method for current densities greater than the critical values as "characteristic" polarisation overvoltages of a metal. As regards speed of commutator, we find, broadly, that the lower the concentration of electrolyte, and more particularly of hydroxyl-ion, the smaller is the speed necessary; or, as we may put it, the greater is the power of the electrode to hold its polarisation. Thus in $4N$-sodium hydroxide nearly 3,000 breaks per minute were necessary, in $N/32$-solution about 1,300 were sufficient; in $2N$-potassium chloride about 1,500 breaks and in $1/32N$-potassium chloride 1,300 breaks sufficed. Temperature seemed to have little effect on the minimum speed of commutator required. The number of breaks and makes employed in the measurements was about 3,600 per minute. The current density was approximately 50 coulombs per second and square centimetre (T., 1923, **123**, 2899, note), the critical current density having been found to vary from slightly more than 10 to slightly more than 20 coulombs per second and square centimetre in passing through various stages of alkalinity from a normal sodium hydroxide to a normal potassium chloride solution. The overvoltage appeared to establish itself almost instantaneously in all the experiments with antimony, and it was found quite safe to take readings half a minute after closing the circuit. The fact that the self-induction of the circuit has no measurable effect on the results has been discussed (*loc. cit.*, p. 2896). In our previous work, the cathode was placed in a porous pot. In many of the experiments now described, the current passing through the solution tended to produce a change of hydroxyl-ion concentration very rapidly. The method adopted in most of the experiments to meet this was to do away with the pot and to mix anode and cathode liquids during the passage of the current by means of a stirrer. In most

cases, the composition of the electrolyte could thus be kept sufficiently constant. In a few cases only was the pot retained, namely, for the sodium hydroxide, the sodium sulphide, and the sodium carbonate experiments. The reference electrode was in every case a hydrogen electrode dipping in electrolyte of the same composition as the liquid under examination, and the overvoltages recorded are the potential differences between this electrode and the cathode as measured on the potentiometer. The hydrogen electrode was always at room temperature. The overvoltage measurements conducted at 70° are therefore subject to a slight correction. This was, however, omitted; for a special series of experiments in which the difference of potential between a calomel electrode at the ordinary temperature and a hydrogen electrode of varying temperature was measured showed that the correction is less than a centivolt. For the purpose of determining hydroxyl-ion concentration, the hydrogen electrode just referred to was put into communication with a saturated calomel electrode and the potential difference between the two measured on the potentiometer. In all the later experiments, a double throw-over switch allowed either the working cathode or the standard electrode to be connected at will in opposite directions through the potentiometer to the hydrogen electrode.

Results.—In the first work performed, four series of experiments were carried out; one in which solutions of sodium hydroxide of various strengths were compared at the ordinary temperature, another in which the same solutions were examined at 70°, a third in which normal solutions, and a fourth in which saturated solutions of various other substances were employed.

It soon became apparent that the overvoltage and the voltage between the saturated calomel electrode and the hydrogen electrode, which we propose to refer to for convenience as p_H voltage, are connected with very considerable accuracy by a linear relation. Indicating the former by ω and the latter by h, we thus have the equation: $\omega = a - bh$, in which a and b are constants. The best value for b in each series of experiments proved to be quite close to 2, whereas a was determined almost identically in all the experiments carried out at the ordinary temperature, but found smaller in the experiments at 70°.

Tables I and II contain these results. The calculated values in Table I are derived from the equation $\omega = 2{\cdot}73 - 2h$; those in Table II from the equation $\omega = 2{\cdot}585 - 2h$. It will be seen that although the wide range of overvoltage from 0·6 to above 1·4 is covered, the differences between calculated and observed values seldom exceed 2 centivolts.

TABLE I.

Temperature 20°. Overvoltage calculated from $\omega = 2{\cdot}73 - 2h$.

Solution.	p_H voltage. h.	Overvoltage ω. Obs.	Calc.
N-NaOH	1·070	0·590	0·59
„ Na_2S (com.)	0·960	0·815	0·81
„ NH_4OH	0·950	0·835	0·83
„ Na_2CO_3	0·940	0·855	0·85
„ Na_2HPO_4	0·786	1·140	1·16
„ $NaHCO_3$	0·750	1·235	1·23
Saturated NaOH	1·100	0·530	0·53
„ Na_2S (com.)	0·965	0·795	0·80
„ NH_4OH	0·956	0·800	0·82
„ Na_2CO_3	0·942	0·850	0·85
„ Na_2HPO_4	0·790	1·160	1·15
„ $NaHCO_3$	0·750	1·235	1·23
„ Na_2SO_4	0·659	1·442	1·41
„ KCl	0·660	1·440	1·41

TABLE II.

Temperature 70°. Overvoltage calculated from $\omega = 2{\cdot}585 - 2h$.

Solution.	p_H voltage. h.	Overvoltage ω. Obs.	Calc.	Solution.	p_H voltage. h.	Overvoltage ω. Obs.	Calc.
$2N$-NaOH	1·065	0·457	0·455	$N/4$-NaOH	1·035	0·515	0·515
N „	1·055	0·475	0·475	$N/8$ „	1·020	0·545	0·545
$N/2$ „	1·045	0·495	0·495	$N/16$ „	1·005	0·575	0·575

TABLE III.

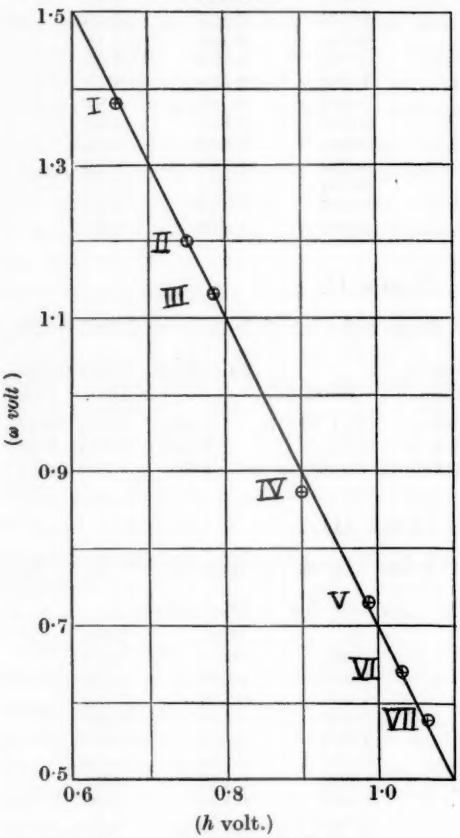
Temperature 20°. Overvoltage calculated from $\omega = 2{\cdot}70 - 2h$.

Solution.	p_H voltage. h.	Overvoltage ω. Obs.	Calc.
$2N$-NaOH	1·062	0·575	0·58
N „	1·050	0·590	0·60
$N/2$ „	1·040	0·621	0·62
$N/4$ „	1·023	0·656	0·65
$N/8$ „	1·006	0·690	0·69
$N/16$ „	0·985	0·726	0·73
$N/3$-NaOH + $2/3N$-Na_2SO_4	1·032	0·640	0·64
N-Na_2CO_3	0·900	0·875	0·90
„ Na_2HPO_4	0·785	1·130	1·13
„ $NaHCO_3$	0·750	1·200	1·20
„ Na_2SO_4	0·655	1·380	1·39
„ KCl	0·655	1·380	1·39
$N/4$-Na_2CO_3	0·900	0·900	0·90
Same solution after electrolysing for various periods	0·915	0·880	0·88
	0·920	0·850	0·85
	0·940	0·815	0·82
	0·950	0·795	0·80
	0·960	0·775	0·78
	0·970	0·760	0·76

The results recorded in Table III were obtained about six months later than those of Table I; a carefully prepared saturated calomel

electrode was employed which was periodically checked by comparison with a $N/10$-calomel electrode and showed the constant difference 0·088 volt. In this series, a porous pot was employed both for the sodium hydroxide and for the sodium carbonate experiments. In the latter case, the experiments were started with a solution of quarter-normal strength. During the passage of the current the hydroxyl-ion concentration increased so that the overvoltage became smaller and the p_H voltage greater. Several pairs of readings were thus obtained which are recorded, the p_H voltage being determined for each pair immediately after the overvoltage. For this purpose, the current was stopped and fresh electrolyte from the porous pot was drawn into the hydrogen electrode chamber. The calculated numbers are here derived from the equation $\omega = 2{\cdot}70 - 2h$, and their agreement with the observed values is excellent, as will be seen. It will be noted, however, that the constant is about 3 centivolts lower than the one employed in Table I. As reference electrode for the earlier experiments, a saturated calomel electrode was employed which had been in stock for some time. Unfortunately, this electrode was accidentally broken, so that it was not possible to check its accuracy by comparison with other standards. It is therefore possible that the small discrepancy may be partly due to an error

FIG. 1.



I, N-Na_2SO_4; II, N-$NaHCO_3$; III, N-Na_2HPO_4; IV, N-Na_2CO_3; V, $N/16$-NaOH; VI, $N/3$-NaOH+$2/3N$-Na_2SO_4; VII, $2N$-NaOH.

in the standard. We think it, however, more likely that it is to be ascribed to some other cause we have not traced fully. The results of Table III have been plotted in Fig. 1, such points being omitted which would have interfered with the clearness of the diagram.

Discussion.

The experiments described have shown that polarisation-overvoltage of antimony in alkaline solution is expressed to a very considerable degree of accuracy by the equation

$$\omega = a - 2h \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which ω and h are overvoltage and p_H-voltage, respectively, and a is a constant depending only on the temperature. Other factors, such as sodium-ion concentration, appear to be without measurable influence, for the equation applies to the most varied electrolytes and also to such mixtures as those of sodium hydroxide and sodium chloride.

The p_H voltage allows us to calculate the hydrogen-ion and therefore the hydroxyl-ion concentration of the solution. Indicating the latter by $\overline{OH}$, we have

$$h = A + B\log_e \overline{OH} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where the constant A is the value of h for a solution in which $\overline{OH} = 1$ and the constant B has the familiar value RT/F. The polarisation-overvoltage we shall consider conditioned by atomic hydrogen dissolved in the cathode. If the gas laws hold, and assuming the overvoltage to be equal to the voltage of a reversible cell, one electrode of which is the working electrode holding atomic hydrogen of the concentration C_h, and the other a similar electrode in which the concentration is C_o and which is in thermodynamic equilibrium with hydrogen of atmospheric pressure, then

$$\omega = B\log_e(C_h/C_o)$$

or

$$\omega = D + B\log_e C_h \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where D is a constant.

We may consider equations 2 and 3 to be independent of the validity of the gas laws if, according to the practice due to G. N. Lewis, we assign the meaning of "activity" to the symbols used for concentrations. Equation (3) expresses likewise the relation of ω to the activity C_h of any other atomic hydrogen that is in thermodynamic equilibrium with the electrode—for example, that dissolved in the electrolyte adjoining the electrode—if the constants C_o and D are correspondingly altered.

Eliminating ω and h from equations 1, 2, and 3, we find after slight rearrangement

$$C_h \times \overline{OH^2} = e^{\frac{a-2A-D}{B}} = \text{constant} \quad . \quad . \quad (4)$$

To interpret this equation we assume that a composite ion of the formula $H(OH)_2''$ or a polymeride is formed in solution. If the speed of formation is sufficiently great and we assume further that the concentration of this ion is maintained in thermodynamic equilibrium with the working electrode, we deduce from equation (4) that the activity and therefore the concentration of the ion maintains a constant value.* We make the further hypothesis that the solubility of such an ion has a limit, and that there is also a supersolubility limit at which it separates without lag in the solid (or liquid) state. Such a solid (or liquid) ion would undoubtedly be highly unstable and when its size has grown to that of a small number of molecules it would decompose as a whole or explode. The free energy required for the production of the surface of a gas-bubble of approximately molecular dimensions would thus be provided by the simultaneous decomposition of a number of ions, and the difficulty, recognised since the time of Helmholtz, connected with the spontaneous formation of such a bubble would be overcome.

* This result, in the deduction of which G. N. Lewis's concept of activity is employed, is independent of the gas laws. The method adopted has the advantage that the ideas and formulæ employed are those most familiar to chemists. A logically and mathematically more direct method, however, consists in proceeding straight from free energy ideas. We shall have proved our result if we can show that the free energy of the ion $H(OH)_2''$ produced reversibly has a constant value independent of the OH' concentration of the solution. We have the free energy equations:

$$\underset{\text{sol.}}{H(OH)_2''} = \underset{\text{sol.}}{H} + 2\underset{\text{sol.}}{(OH)'}; \quad \underset{\text{atm.}}{H} = \underset{\text{sol.}}{H^{\cdot}} + (G + Fh); \quad \underset{\text{sol.}}{H^{\cdot}} + \underset{\text{sol.}}{OH'} = H_2O; \text{ and}$$

$$\underset{\text{atm.}}{H} + F\omega = \underset{\text{sol.}}{H}.$$

In these equations, the chemical symbols indicate free energies of atomic (molecular ionic) proportions in grams of the substances at the constant temperature considered; h and ω are p_H voltage and overvoltage, respectively, F is one faraday, and G a constant. The abbreviation sol. under a symbol expresses the fact that the molecular species indicated is in solution and that its free energy is therefore variable; the symbol H, on the other hand, expresses the free energy of 1 gram of hydrogen under atmospheric pressure and therefore is constant. Eliminating the variables H (sol.), $H^{\cdot}$ (sol.), OH' (sol.) from these equations, we find:

$$\underset{\text{sol.}}{H(OH)_2''} = 2H_2O + 2G - \underset{\text{atm.}}{H} + F(\omega + 2h).$$

In the expression on the right-hand side of this result, all the quantities except ω and h are constants. According to our empirical equation (1), however, $\omega + 2h$ equals the constant a, therefore the whole expression is a constant, which is what we set out to prove.

We were at first disposed to look for the explanation of equation 4 in the formation on the surface of the electrode of an unstable (explosive) antimony compound having the formula $Sb_m[H(OH)_2]_n$. More careful consideration, however, showed that such an assumption is untenable, for if the conditions are such that the free energy of an ion of the kind we are considering has a constant value in various solutions, the free energy of a compound such as $Sb_m[H(OH)_2]_n$ would be constant only if the work required to force the ion from the solution into contact with the metal through the drop of potential at the boundary were in every instance the same. With the overvoltages we have found, this is, however, not the case, for the metal is the more negative with respect to the solution during the passage of the current the higher the overvoltage, that is, the lower the hydroxyl-ion concentration. Another process of reasoning by means of which the same deduction is reached is to consider directly the formation of the compound $Sb_m[H(OH)_2]_n$. In such a consideration, the concentration to be assigned to OH′ is not the concentration in the body of the solution, but the much smaller one in the layer in immediate contact with the cathode, separated from the body of the solution by the potential drop electrolyte-cathode.

We are thus led to a conclusion which is at total variance with the ideas with which we started this work. We find that the antimony plays an indifferent part in the evolution of hydrogen at the cathode and that the production of stibine is not a primary, but a secondary phenomenon resulting from the explosive decomposition of the ion $H(OH)_2''$. Another important deduction we draw is that the relation we have found to hold between polarisation-overvoltage and p_H voltage for antimony in alkaline solution should hold equally for other metals which play an indifferent part as cathodes. We hope to return to this matter in a future communication.

It may be useful to summarise here the hypotheses we have made in the course of this discussion. They are (1) An ion $H(OH)_2''$ is produced in solution from its component parts with practically infinite velocity, and this ion has a definite solubility, and more particularly a definite supersolubility limit. (2) Polarisation-overvoltage is determined by the concentration of hydrogen dissolved in, or adsorbed by, the surface of the electrode in accordance with the usual thermodynamic considerations. (3) The hydrogen dissolved in the working cathode is in thermodynamic equilibrium with hydrogen dissolved in the layer of electrolyte immediately outside the double layer separating the metal from the solution. The accuracy of the empirical formula we have found will depend

on the accuracy with which this hypothesis is obeyed. The possibility must be envisaged that there may be a lag in this equilibrium, variations of which may interfere with the constancy of overvoltage values. Hypothesis (3) appears to involve the further hypothesis (4). Hydrogen is deionised simultaneously on the electrode, throughout the double layer, and immediately beyond it, that is, free electrons travel directly from the cathode into the solution over this range during the passage of the current.

Summary of Results.

The characteristic polarisation-overvoltage, ω, of an antimony cathode in alkaline solution is determined by the equation $\omega = a - 2h$, in which h is the p_H voltage, and a a constant depending only on the temperature. This result, as well as the formation of gas bubbles, may be explained by the assumption that an ion, $H(OH)_2''$, exists which has a definite supersolubility limit. When a sufficient number of these ions have assembled in the solid (or liquid) state to produce the energy necessary for the formation of a gas bubble, they will decompose simultaneously (explode). The conclusion has been drawn that the identical overvoltage–p_H voltage relation should be found with other metals that act as indifferent cathodes in alkaline solution.

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XXII.—*The Additive Formation of Four-membered Rings. Part IV. The Influence of Temperature on the Tendency towards Self-addition of the Nitroso-group.*

By CHRISTOPHER KELK INGOLD and HENRY ALFRED PIGGOTT.

IN Part I of this series (Ingold and Piggott, T., 1922, **121**, 2793) the hypothesis was adopted that all double-bonded substances tend, when in the dissolved or liquid state, towards the establishment of equilibria with their dimeric forms

$$2A{:}B \rightleftharpoons \begin{matrix} A—B \\ | \quad | \\ B—A \end{matrix}$$

So far as observation has yet progressed with regard to the five types of double bond now under examination (C:C, C:O, N:N, N:O, C:N) no reason has arisen to doubt the truth of this generalisation. In some cases, in most ethylenic compounds, for instance, the

equilibrium may be only slowly attained at the more available temperatures; in others, for example, in most azo-compounds, the equilibrium may be very one-sided; but in others again the equilibrium may be of a measurable order and rapidly established at temperatures quite near to the ordinary temperature. The last has proved to be the case with many azomethines; in Part I certain reactions depending fundamentally on this equilibration were shown to take place readily at the ordinary temperature, and in Part II (T., 1923, **123**, 2745) an instance was given in which the equilibrium

$$2\dot{N}{:}\dot{C}- \rightleftharpoons \begin{matrix} -N-C< \\ >C-N- \end{matrix}$$

changes from right to left practically completely for a rise of temperature of 250°.

From this and other evidence it may be assumed that the heat of formation of the four-membered rings from the double-bonded compounds is, in general, positive; and that a rise of temperature will shift the equilibrium in favour of the double-bonded molecules. Temperature is evidently a most important factor in determining the stability of four-membered rings.

Special interest attaches to nitroso-compounds in this connexion, because the group N:O is chromophoric, and it should be possible to follow the effect of temperature on the equilibrium

$$\underset{\text{(blue)}}{2\dot{N}{:}O} \rightleftharpoons \underset{\text{(colourless)}}{\begin{matrix} -N-O \\ O-N- \end{matrix}} \quad . \ . \ . \ . \ . \quad (A)$$

with the aid of the colorimeter.

It is well known that most of the simpler aromatic nitroso-compounds, although colourless in the solid state, yield blue solutions, in some of which the solute possesses the normal molecular weight, whilst in others it has a higher value, amounting to 1·7 times the normal in the case of nitrosomesitylene. A plausible interpretation is furnished by the suggestion contained in the preceding paragraph, and is supported by the fact that normal molecular weights are usually obtained in solutions possessing the deepest blue colour. Although plausible, it cannot, however, be assumed to be the correct explanation without further evidence. The reversible reaction

$$\underset{\text{(blue)}}{3\dot{N}{:}O} \rightleftharpoons \underset{\text{(colourless)}}{\begin{matrix} & N & \\ O & & O \\ -N & & N- \\ & O & \end{matrix}} \quad . \ . \ . \ . \ . \ . \ . \quad (B)$$

would be equally in agreement with the facts at present known, as indeed would any reversible polymerisation involving a colourless polymeride; and analogy provides no clear distinction between mechanism (*A*) and mechanism (*B*), since many analogies could be instituted in favour of either. Hence, before any information can legitimately be sought from colorimetric measurements as to the influence of temperature on the tendency towards self-addition of the nitroso-group, it must first be inquired whether observations with the colorimeter can determine without ambiguity the nature of the reaction on which the colour change depends.

In the first place, it should be noted that for the majority of aromatic nitroso-compounds the equilibrations between the blue and the colourless individuals take place much too rapidly at convenient temperatures to enable the "order" of the reaction to be determined by any of the usual physico-chemical methods, or indeed by any method depending on the time-variation of the colour at constant temperature. It is possible, however, to employ for the purpose temperature-variation under equilibrium conditions, and a method for doing this has been elaborated in the present case.

Let the degree of polymerisation be represented by n, which may be any number, although analogy suggests 2 or 3 as the most probable value; and let the dissociation of the polymeride be attended by the evolution of q gram-calories per gram-molecule. Let a be the molecular-concentration in which the polymeride would occur if all the nitroso-compound were polymerised, and let $a - x$ be the molecular concentration of the polymeride after equilibrium has been established at $T°$. The temperature-variation of x for slow changes of T will then be given by the equations

$$\delta \log_e K/\delta T = -q/RT^2 \text{ and } K = n^n x^n/(a - x),$$

that is, by

$$\log_e \frac{n^n x^n}{a - x} = \frac{q}{RT} + C \quad . \quad . \quad . \quad . \quad . \quad \text{(i)}$$

Neglecting thermal expansion, the concentrations of each substance may be regarded as proportional to the actual weight present in equilibrium at the different temperatures, and in the case of the nitroso-compound this will be proportional to the scale-reading, v, which measures the intensity of the blue colour; that is, nx is proportional to v. Let k be a constant defined by $nx = kv$ and let V be a hypothetical scale reading connected with a by the relation $na = kV$. Then equation (1) becomes

$$\log_{10}\frac{v^n}{V-v}=\frac{q}{2{\cdot}303RT}+\frac{C-\log_e nk^{n-1}}{2{\cdot}303},$$

or, since n, k, q, and R are constants,

$$\log_{10}\frac{v^n}{V-v}=\frac{\beta}{T}+\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

where

$$q=4{\cdot}571\ \beta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iii)}$$

If three values of v are known, say v_1, v_2, and v_3, corresponding with T_1, T_2, and T_3, then, eliminating α and β, we find the following equation for n :

$$n=\frac{\dfrac{T_2-T_1}{T_3-T_1}\cdot\dfrac{T_3}{T_2}\cdot\log_{10}\dfrac{V-v_3}{V-v_1}-\log_{10}\dfrac{V-v_2}{V-v_1}}{\log_{10}\dfrac{v_1}{v_2}-\dfrac{T_2-T_1}{T_3-T_1}\cdot\dfrac{T_3}{T_2}\cdot\log_{10}\dfrac{v_1}{v_3}} \quad . \quad . \quad \text{(iv)}$$

This equation is best computed by the graphical method indicated in the experimental portion of this paper. By taking, not three, but five or six observations as a basis of calculation, a series of values of n can be found, all of which lie close to 2, their mean being 2·0 to two significant figures. That is to say, the reaction under discussion is a reversible bimerisation to which type A conforms, and the theoretical expression with which the observations must be compared is of the form (v), this form being determined without ambiguity by the observations themselves.

$$\log_{10}\frac{v_2}{V-v}=\frac{\beta}{T}+\alpha \quad . \quad . \quad . \quad . \quad . \quad \text{(v)}$$

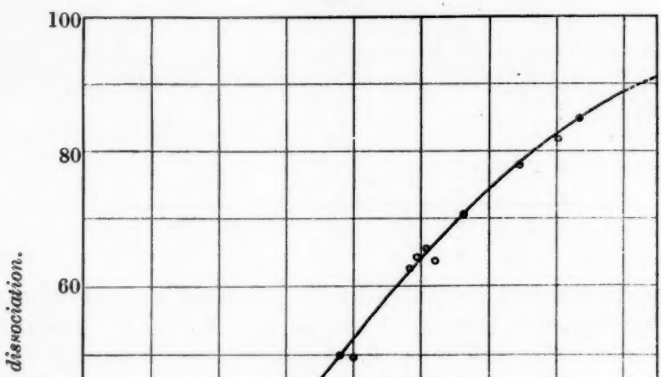
When the data, which refer throughout to nitrosomesitylene in benzene solution, are compared with the graph of equation (v), two observations being used to evaluate the constants α and β, the results exhibited in Fig. 1 * are obtained. Most of the points representing observations lie within 1 per cent. of the theoretical curve, and nearly all within 2 per cent. Since no readings have been rejected, and the complete set includes a few made under imperfect optical conditions, an accuracy of about 1—2 per cent. can be claimed; and from the irregular distribution of the deviations it must be concluded that the agreement with theory is well within the limits of experimental accuracy.

The diagram shows that the dissociation of the dioxadi-imine ring (this vol., p. 88) varies from 18 per cent. to 89 per cent.

* Excepting that $100v/V$ has been plotted in place of v, and $T-273{\cdot}1$ in place of T (see p. 174).

between the freezing point and the boiling point of benzene—figures which are a quantitative expression of the fact, which had already become apparent from many incidental observations, that quite a moderate change of temperature may exert a very large influence on the formation and stability of four-membered rings.*

FIG. 1.



EXPERIMENTAL.

Mesidine.—This was prepared by a modification of Hofmann's method (*Ber.*, 1872, **5**, 706, 715). A mixture of carefully purified dimethylaniline (35·7 grams) and methyl iodide (34 grams), which rapidly set to a white, crystalline mass, was heated in a sealed tube so that the thermometer registered 200° after one hour, 260° after three hours, and 290—300° for a further four hours. When cold, the contents of the tube were extracted with boiling water, acidified (if necessary) with hydrochloric acid, and distilled in

* For the thermal effect accompanying the change, see p. 175.

steam. When no more oil passed over, the residue was rendered strongly alkaline with sodium hydroxide, and again distilled in steam until the distillate was no longer alkaline. The combined alkaline distillates were acidified with hydrochloric acid and evaporated until crystallisation commenced. On cooling, a semi-solid mass was obtained which was filtered; and the residue was washed with 95 per cent. alcohol and crystallised from this solvent. It separated in long, colourless needles which decomposed and volatilised without melting. The purity was controlled by the melting point of the crude acetyl derivative obtained by adding acetic anhydride to an alkaline solution of the hydrochloride.

In this way 55 grams of mesidine hydrochloride were obtained from 348·5 grams of phenyltrimethylammonium iodide. The salt was dissolved in an excess of sodium hydroxide and the base extracted with ether, dried in ether solution with potassium carbonate, and distilled, the fraction, b. p. 226—230°, being collected for the preparation of the nitroso-compound.

The acetyl derivative crystallises from alcohol or dilute acetic acid in colourless prisms, m. p. 210—212° (Found : C = 74·53; H = 8·58. Calc., C = 74·52; H = 8·54 per cent.).

Nitrosomesitylene.—A solution of 37 grams of ammonium persulphate in 30 c.c. of concentrated sulphuric acid was poured on to 500 grams of ice, almost neutralised with crystallised sodium carbonate (150 grams), and mechanically stirred while 10 grams of mesidine were added, followed by sodium carbonate solution, the addition of which was repeated at intervals to maintain the liquid faintly alkaline. After one and a half hours, the brown solid was collected, washed with hydrochloric acid, and rubbed with light petroleum to dissolve gummy impurities. The white, crystalline residue separated from 95 per cent. alcohol in glistening, colourless, rhombic plates, which melted at 122—123° to a bright bluish-green liquid [Pechmann and Nold (*Ber.*, 1898, **31**, 561) give m. p. 129°, but quote the figure 121·5—122·5° privately communicated to them by Bamberger] (Found : C = 72·36; H = 7·45. Calc., C = 72·44; H = 7·44 per cent.). The yield was 30 per cent. of the theoretical.

Colorimetric Measurements.—These observations were made with a colorimeter of the usual type adapted so that the tube containing the solution of nitrosomesitylene could be maintained at any desired temperature by means of a water-bath. The comparison tube was arranged so that readings could be obtained either by a measurement of depth, or by running in the colour-standard from a burette. The latter method was usually employed in taking a series of readings for ascending temperatures, and the former method for descending temperatures.

The following data refer to a 3·00 per cent. solution of nitrosomesitylene in benzene.

$T(=273{\cdot}1+t)$.	v.	% dissociation = $100v/V$. Obs.	Calc.
Set 1. Ascending temperatures.			
279·3°	3·44	18·5	18·9
287·7	4·70	26·1	25·0
296·9	6·10	33·8	33·6
306·1	8·03	44·6	43·9
321·5	11·27	62·6	62·2
329·3	12·73	70·7	70·6
Set 3. Ascending temperatures.			
290·5	4·70	26·1	27·4
300·1	6·32	35·1	36·9
311·1	9·00	50·0	50·0
322·6	11·58	64·3	63·4
337·2	14·04	78·0	78·2
348·1	15·50	86·1	86·0

$T(=273{\cdot}1+t)$.	v.	% dissociation = $100v/V$. Obs.	Calc.
Set 2. Descending temperatures.			
323·9°	11·80	65·6	65·0
313·1	8·95	49·7	52·5
303·3	7·53	41·8	40·4
293·1	5·30	29·4	29·8
282·1	3·50	19·5	20·6
Set 4. Descending temperatures.			
343·4	14·75	81·9	82·7
325·1	11·48	63·8	66·1
302·3	7·20	40·0	39·2
296·4	5·73	31·8	33·0
291·7	5·10	28·3	28·3

The observed and calculated values of the percentage dissociation were obtained in the manner described below, and are exhibited graphically on Fig. 1. Fourteen of the twenty-two differences lie within 1 per cent., and twenty within 2 per cent.

Order of the Reaction.—This was determined with the aid of formula (iv) (p. 171) and certain data taken from the list given above. The best method of computation is a graphical one, the observations being taken in sets of three and a series of curves for the dependence of n on V constructed using the formula. For instance, the three observations $T = 296{\cdot}9°$, $v = 6{\cdot}1$; $T = 311{\cdot}1°$, $v = 9{\cdot}0$; and $T = 348{\cdot}1°$, $v = 15{\cdot}5$ lead to the values

V	16·5	17·0	17·6	18·0	19·0	20·0
n	3·83	2·92	2·26	1·96	1·41	1·08

Replacing the third observed point by $T = 337{\cdot}2°$, $v = 14{\cdot}04$, one finds

V	17·0	18·0	19·0	20·0
n	2·54	1·97	1·50	1·22

If the corresponding graphs are constructed, it will be seen that they intersect at $V = 17{\cdot}95$, $n = 1{\cdot}98$. Similarly, by taking other data, a series of curves can be constructed all of which pass close to the point $V = 18{\cdot}0$, $n = 2{\cdot}0$. Of course, the degree of coincidence amongst the points of intersection can be greatly improved by taking results from a mean curve drawn through the observations instead of the observations themselves, but the values of V and n so obtained are the same to the number of significant figures quoted.

Calculation of the Percentage Dissociation.—This is obtained from the relation $p = 100\,v/V$, in which V has the value 18·0. The figures

quoted in the third column of the table have been calculated from this formula.

The Theoretical Formula (v).—Using formula (v) in conjunction with any two observations, the constants α and β can be calculated. As in all cases of this kind, the form and disposition of the curve are not very sensitive to small changes of β, provided that α is suitably adjusted. Since the determined values of β all lay close to -3000, this rounded figure was selected and α was calculated to suit. Subtracting $\log_{10}(V/100)$ from α, the following equation is obtained,

$$\log_{10}\frac{p^2}{100-p} = 11{\cdot}34 - \frac{3000}{t+273{\cdot}1},$$

from which the values given in the fourth column of the table have been calculated.

The Heat of Dissociation.—From formula (iii) the heat absorbed during the dissociation of one gram-molecule of dimeric nitrosomesitylene is evidently about 13,700 gram-calories. Since practically complete dissociation takes place on melting, the latent heat of fusion must involve a contribution of about 46 gram-calories per gram, arising solely from the change in molecular weight. The fact that the majority of aromatic nitroso-compounds must possess very large latent heats of fusion becomes obvious on merely taking their melting point in a capillary tube; and it is impossible to work with them without noticing the large absorptions of heat which occur on dissolution in organic solvents—an effect evidently due to their negative heats of dissociation.

Comparison with Determinations of Molecular Weight.—Bamberger, Rising, and Demuth (*Ber.*, 1900, **33**, 3634; 1901, **34**, 3879) have recorded a number of determinations of the molecular weight of nitrosomesitylene at the freezing point of benzene. The eleven observations are not very concordant, but the mean of them all is 246 for a 2·0 per cent. solution. Fig. 1 shows that in 3·0 per cent. solution in benzene dissociation occurs to the extent of 18·0 per cent. The dissociation in 2·0 per cent. solution is therefore given by

$$\frac{p'^2}{100-p'} = \frac{3{\cdot}0}{2{\cdot}0}\cdot\frac{18^2}{100-18},$$

from which we find $p' = 21{\cdot}6$ per cent. The molecular weight corresponding with this degree of dissociation is 245.

Only two observations of the molecular weight at the boiling point of benzene have been recorded: the mean of these is 155·4 for a 1·51 per cent. solution. Fig. 1 shows that at 80° in a 3·0 per cent. solution the dissociation amounts to 89 per cent. Calculating

as before, we find that in a 1·51 per cent. solution the dissociation would be 94 per cent. The corresponding molecular weight is 154. This agreement is evidently accidental, since taking the average of only two values is not a satisfactory way of eliminating observational error.

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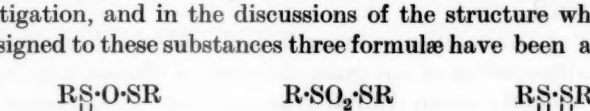
XXIII.—*The Constitution of Disulphoxides. Part I.*

By SAMUEL SMILES and DAVID TEMPLETON GIBSON.

THE reactions of the disulphoxides have been the subject of frequent investigation, and in the discussions of the structure which should be assigned to these substances three formulæ have been advocated :



(I.) (II.) (III.)

The first of these seems to have been based (Fromm, *Ber.*, 1906, **39**, 3311; Gutmann, *Ber.*, 1914, **47**, 635) on somewhat ambiguous evidence and has little to be said in its favour, whilst the arguments against it, which have been summed up by Fries (*Ber.*, 1914, **47**, 1195), seem insuperable. Their main strength lies in the fact that, the anhydrides of sulphinic and of sulphenic acids being known, it is possible with confidence to predict the properties of a mixed anhydride of the two as represented by this formula. These are not at all in accord with the properties of the disulphoxides. In fact, at present the main issue lies between the second and the third formula quoted. Of these, the former was advocated by Otto and his collaborators as the result of a thorough examination of this group of substances. This unsymmetrical formula represents the disulphoxides as esters of thiosulphonic acids. Since the chief facts on which this view was based seem to have been lost sight of in later discussions, they are summarised as follows :

(1) Warm solutions of alkali hydroxide give a sulphinic acid and disulphide and sometimes a mercaptan (*Ber.*, 1886, **19**, 1235).

(2) Zinc dust in alcohol yields the zinc sulphinate with zinc mercaptide (*Ber.*, 1877, **10**, 2181; 1878, **11**, 2073; 1882, **15**, 121; 1887, **20**, 2079).

(3) Potassium sulphide yields the mercaptide and thiosulphonate or sulphinate (*Ber.*, 1886, **19**, 3129; 1887, **20**, 2079; 1892, **25**, 1477).

(4) A mercaptan or mercaptide gives a sulphinic acid or a salt thereof and a disulphide (*loc. cit.*).

(5) Finally, Otto synthesised (*loc. cit.*) alkyl thiosulphonates, but in the case where the corresponding disulphoxide was available no close physical comparison was possible, since both substances were liquids which decomposed on distillation. However, the reactions of these synthetical products so closely resembled those of the disulphoxides that identity in structure of the two series was confidently deduced.

This view of the constitution of the disulphoxides has in recent years given place to that represented by the symmetrical formula (III), according to which these compounds are to be regarded as true α-disulphoxides. The suggestion that these substances should be so regarded seems to have first arisen from the observation that they are formed by the reaction of hydrogen peroxide with a disulphide. It had been found that with monosulphides this reagent yielded sulphoxides and in none of the cases then studied had a sulphone been obtained. The objection to this argument is obvious; but it need not now be discussed, since more recent work has shown that sulphones may be formed by this reagent (see, for example, Lesser, *Ber.*, 1923, **56**, [*B*], 1647). The evidence which is regarded as favouring this disulphoxide structure and as excluding the thiosulphonate arrangement is drawn mainly from the fact that these compounds are easily reduced by hydrogen iodide (Hinsberg, *Ber.*, 1908, **41**, 2836, 4294; 1909, **42**, 1278) or even by hydrogen bromide (Fries, *loc. cit.*), disulphides being formed, or in some cases with the latter reagent, sulphur bromides. It has been argued (Hinsberg, *loc. cit.*; Fries, *loc. cit.*) that the sulphone group could not be reduced by these reagents, whilst sulphoxide groups are easily attacked. At the same time, objection has been raised (Hinsberg, *loc. cit.*) to the evidence from the action of alkali hydroxide on the grounds that it may be explained by either formula (Gutmann, *loc. cit.*), whilst it has been further pointed out that the syntheses effected by Otto are not decisive, for the constitution of the alkali thiosulphonates is not firmly established (Gutmann, *Ber.*, 1908, **41**, 3351). The force of the latter arguments may be conceded, but the conclusions based on the reduction of the disulphoxides by the halogen acids appear open to criticism. Thus Fischer (*Ber.*, 1915, **48**, 93, 360) has pointed out the remarkable difference in the reactivity of the sulphonic acids and sulphonamides; the former resist the action of hydrogen iodide, whilst the latter are readily attacked at 100°, yielding the disulphide or mercaptan. Moreover, disulphones may be reduced by hydrogen iodide to the disulphide under the same conditions applied to the

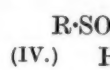
sulphonamides. Evidence of this kind clearly shows that, as might be expected, the reactivity of the sulphone group varies with the nature of the groups to which it is attached. A more emphatic criticism arises from the fact that the evidence is quite indecisive, since the formation of disulphide from disulphoxide may be interpreted in two ways which respectively invoke persistence or rupture of the dithio-group during the process. Those who claim that this reduction indicates the symmetrical and is incompatible with the unsymmetrical formula rely on the assumption that the process is direct and that the dithio-system is not ruptured. On the other hand, if fission of this group takes place, the sulphinic acid and sulphur halide or related disulphide would, according to the thiosulphonate formula, be at first formed; but the fact that the sulphinic acid has not been discovered among the products has no significance, for these acids are so easily reduced by hydrogen iodide or bromide to the disulphide or sulphur halide (Fries, *loc. cit.*; Cleve, *Ber.*, 1888, **21**, 1099) that they could scarcely be expected to occur among the products of the reaction. Moreover, it should be noticed that the latter interpretation of the reduction is in accord with the reactions of the disulphoxides studied by Otto, which clearly show that the union between the sulphur groups in the disulphoxides is very easily broken. For these reasons the results hitherto obtained from the reduction of the disulphoxides by halogen acids are ambiguous, and the symmetrical structure which relies on this reaction for its chief support is far from firmly established. Reviewing other evidence which is at present available, it seems that, on the contrary, there is much to be said for the unsymmetrical structure. The results of the action of zinc dust and of potassium sulphide seem unequivocal, and to these must be added the reduction by sodium arsenite (Gutmann, *loc. cit.*), which yields the sulphinic acid and mercaptan, as well as the synthesis effected by Zincke (*Annalen*, 1912, **391**, 67) from a sulphur halide and a silver sulphinate:

$$R{\cdot}SO_2Ag + ClSR = AgCl + R{\cdot}SO_2{\cdot}SR.$$

All these point to the unsymmetrical distribution of oxygen in the molecule.

In the experiments described in the following pages attention has been directed to the action of mercaptans with disulphoxides in order to determine whether this also should be included among the reactions indicating the unsymmetrical structure. The reaction in question leads (Otto, *loc. cit.*) to a sulphinic acid and a disulphide. This result might be simply interpreted on the basis of either formula; according to the thiosulphonate structure simple fission takes place

(IV), whilst according to the disulphoxide structure the sulphinic acid might be supposed to be formed by oxidation of the mercaptan (V).



(IV.)

(V.)

If now a mercaptan be chosen containing a group R′ different from that contained by the disulphoxide, it is clear that according to (IV) a mixed disulphide should result together with a sulphinic acid containing the group R of the disulphoxide, whilst according to (V) the symmetrical disulphide $(RS)_2$ and the sulphinic acid $R'\cdot SO_2H$ must be obtained. It has been found that the reaction proceeds according to the first of the schemes mentioned, high yields of the sulphinic acid $R\cdot SO_2H$ being obtained, and in many cases the mixed disulphide, RS·SR′, when crystalline, has been isolated in a pure condition. The sulphinic acid corresponding to the mercaptan used was not detected in any of the products. Hence it is evident that in this, as well as in the reactions previously mentioned, the disulphoxides behave in accordance with the unsymmetrical formula (II).

Experiments are now in progress to obtain more precise information on the course of the reducing action of halogen acids as well as on the possibility of intramolecular change between the two types of structure (compare Hilditch, T., 1910, **97**, 1098; Fries, *loc. cit.*; Hinsberg, *loc. cit.*); and it is hoped that decisive evidence of the constitution of these substances will be forthcoming.

Experimental.

The mercaptans used in these experiments were prepared as usual by the reduction of the sulphonyl chlorides, and the sulphinic acids required for purposes of identification and as a source of the disulphoxides were furnished by reduction of the sulphonyl chlorides with aqueous sodium sulphite of varying strength. For the preparation of the disulphoxides required, the method recommended by Hilditch (*loc. cit.*) was found to be superior to any other. These methods are illustrated by the following cases of the 2 : 5-dichloro-derivatives which have not previously been recorded in literature.

2 : 5-*Dichlorobenzenesulphinic Acid*, $C_6H_3Cl_2\cdot SO_2H$. — 2 : 5-Dichlorobenzenesulphonyl chloride (100 grams) (Stewart, T., 1922, **121**, 2555) was shaken with a cold solution of sodium sulphite (300 grams) and sodium hydroxide (20 grams) in a litre of water.

When the sulphonyl chloride had dissolved, the solution was filtered, and acidified with concentrated sulphuric acid. The required sulphinic acid (75 grams) was precipitated in the crystalline state, and after purification from hot water it melted at 122° (Found : Cl = 33·6. $C_6H_4O_2Cl_2S$ requires Cl = 33·65 per cent.).

2 : 5 : 2′ : 5′-*Tetrachlorodiphenyl Disulphoxide*, $(C_6H_3Cl_2)_2S_2O_2$.—Two litres of water containing two drops of concentrated sulphuric acid, ten drops of concentrated hydrogen iodide, and the requisite sulphinic acid (50 grams) were heated on the water-bath for four hours, sufficient sulphurous acid being added at intervals to decolorise the liquid. The insoluble product was collected and triturated with aqueous sodium hydroxide; the residue (20 grams) was then recrystallised from light petroleum, when the required disulphoxide was obtained in colourless needles, m. p. 128°. The substance is sparingly soluble in cold alcohol and readily soluble in acetone (Found : C = 37·0; H = 1·6. $C_{12}H_6O_2Cl_4S_2$ requires C = 37·11; H = 1·55 per cent.).

3 : 3′-*Dicarboxydiphenyl disulphoxide*, $(C_6H_4{\cdot}CO_2H)_2S_2O_2$, was prepared in a similar manner. The product melted at 229° and was evidently in a purer condition than that (m. p. 220°) previously obtained (T., 1921, **119**, 1792) by treating the disulphide with iodine and aqueous sodium hydroxide.

In studying the action of mercaptans with disulphoxides, the method employed was to add a solution of the sodium mercaptide in alcohol to an equimolecular proportion of the disulphoxide contained by the same solvent. The majority of the alcohol was then evaporated in an atmosphere of nitrogen, and the residue was mixed with water, from which the insoluble disulphide was removed. The sulphinic acid was liberated from the aqueous solution of its sodium salt, collected by extraction with a suitable solvent, and then identified in the usual manner. In the earlier experiments, which were conducted with the sodium mercaptides, it was found that, whilst the sulphinic acid formed was invariably homogeneous and consisted entirely of that derived from the disulphoxide employed, the unsymmetrical disulphide was sometimes contaminated with the two corresponding symmetrical compounds. This circumstance is undoubtedly due to reaction of the mercaptide with the unsymmetrical disulphide, the case being analogous to the behaviour of the latter substance with sodium sulphide which effects their reduction. Attention was first directed to this behaviour by Lecher (*Ber.*, 1920, **53**, 591), who found in it an obstacle to the preparation of mixed disulphides from sodium mercaptides and sulphenyl chlorides, since the required unsym-

metrical disulphide at first formed was subsequently attacked by the mercaptide,

$$RS{\cdot}SR' + R{\cdot}SNa = RS{\cdot}SR + NaS{\cdot}R',$$
$$RS{\cdot}SR' + R'{\cdot}SNa = R'S{\cdot}SR' + NaS{\cdot}R,$$

with the result that the symmetrical disulphides were formed; but by using the mercaptan in place of the sodium derivative the unsymmetrical disulphide could be readily obtained. In view of this experience the later experiments were conducted with the mercaptans, with the result that the yields of the mixed disulphides were greatly improved. The results of the experiments are collected in the following table. In the third column the sulphinic acids formed from the disulphoxides and mercaptans are given together with the yields in which they were isolated. Owing to inevitable errors in the method of isolation, the amounts quoted are undoubtedly smaller than those actually formed, especially in cases such as the action of β-naphthyl mercaptan with diphenyl disulphoxide, where the quantity of the reactants taken was somewhat less than usual.

	Disulphoxide.	Mercaptan.	Sulphinic acid.	Disulphide.
1	Di-*p*-tolyl disulphoxide.	*p*-Tolyl mercaptan.	*p*-Toluenesulphinic acid : 90 per cent.	Di-*p*-tolyl disulphide.
2	Diphenyl disulphoxide.	Phenyl mercaptan.	Benzenesulphinic acid.	Diphenyl disulphide.
3	Di-*p*-tolyl disulphoxide.	4-Methoxytoluene 3-mercaptan.	*p*-Toluenesulphinic acid : 84 per cent.	A liquid : not purified.
4	Di-*p*-tolyl disulphoxide.	2 : 5-Dichlorophenyl mercaptan.	*p*-Toluenesulphinic acid : 84 per cent.	2 : 5-Dichloro-4′-methyldiphenyl disulphide.
5	2 : 5 : 2′ : 5′-Tetrachlorodiphenyl disulphoxide.	*p*-Tolyl mercaptan.	2 : 5-Dichlorobenzenesulphinic acid : 93 per cent.	A mixture : not separated.
6	Diphenyl disulphoxide.	2-Naphthyl mercaptan.	Benzenesulphinic acid : 60 per cent.	Phenyl-2-naphthyl disulphide.
7	Dicamphoryl-β-disulphoxide.	2 : 5-Dichlorophenyl mercaptan.	Camphor-β-sulphinic acid : 91 per cent.	A liquid : not purified.
8	3 : 3′-Dinitrodiphenyl disulphoxide.	2 : 5-Dichlorophenyl mercaptan.	3-Nitrobenzenesulphinic acid : 90 per cent.	2 : 5-Dichloro-3′-nitrodiphenyl disulphide.
9	Di-*p*-tolyl disulphoxide.	9-Anthryl mercaptan.*	*p*-Toluenesulphinic acid : 72 per cent.	9-Anthryl-4-tolyl disulphide.
10	3 : 3′-Dicarboxydiphenyl disulphoxide.	*p*-Tolyl mercaptan.	3-Sulphinobenzoic acid.	3-Carboxyphenyl-4′-tolyl disulphide.

* We are indebted to Mr. E. Barnett for a pure specimen of this mercaptan.

The properties of the unsymmetrical disulphides encountered are summarised as follows :

2 : 5-*Dichloro*-4'-*methyldiphenyl disulphide* (obtained from No. 4), when recrystallised from light petroleum, was obtained in colourless needles, m. p. 71—72° (Found : C = 51·6; H = 3·2; Cl = 23·5. $C_{13}H_{10}Cl_2S_2$ requires C = 51·82; H = 3·3; Cl = 23·58 per cent.). Mixtures of this disulphide with either symmetrical disulphide or with an equimolecular mixture of these melted indefinitely at lower temperatures. In No. 5, where the alternative components were taken, the disulphide product could not be resolved into definite substances by crystallisation from the several solvents employed.

Phenyl-2-*naphthyl disulphide* was formed in No. 6 together with a small quantity of di-β-naphthyl disulphide. It melted at 74—75° (Found : C = 71·5; H = 4·3; S = 24·1. $C_{16}H_{12}S_2$ requires C = 71·6; H = 4·5; S = 23·9 per cent.). Lecher (*Ber.*, 1922, **55**, 1480) has recorded 75° as the melting point of this substance.

2 : 5-*Dichloro*-3'-*nitrodiphenyl disulphide* (obtained from No. 8) separated from methyl alcohol in colourless needles, m. p. 89—91° (Found : N = 4·2; Cl = 21·7. $C_{12}H_7O_2NCl_2S_2$ requires N = 4·2; Cl = 21·4 per cent.). Mixtures of this disulphide with an equimolecular mixture of the two symmetrical compounds or with each taken alone melted indefinitely and at lower temperatures than either component.

9-*Anthryl*-4-*tolyl disulphide* (obtained from No. 9) separated from light petroleum in bright yellow needles, m. p. 98—99° (Found : C = 75·7; H = 4·5; *M* = 341, 346. $C_{20}H_{16}S_2$ requires C = 75·9; H = 4·8 per cent.; *M* = 332).

3-*Carboxyphenyl*-4-*tolyl disulphide* (obtained from No. 10) separated from acetic acid in small, colourless crystals, m. p. 140° (Found : C = 61·0; H = 4·4; S = 23·4. $C_{14}H_{12}O_2S_2$ requires C = 60·9; H = 4·3; S = 23·2 per cent.). The behaviour of this substance with alkalis is interesting. The clear solution in aqueous sodium carbonate rapidly became turbid when it was warmed owing to separation of tolyl disulphide. On acidifying the solution after this disulphide had been removed, 3-mercaptobenzoic acid was liberated. With aqueous sodium hydroxide, this decomposition takes place slowly at the ordinary temperature. It is evident that the substance suffers hydrolysis at the dithio-group like the symmetrical *m*-dithiobenzoic acid (T., 1921, **119**, 1794) and *o*-carboxyphenyldithioglycollic acid (T., 1922, **121**, 89), the fragments containing the thiotolyl residues reuniting to form the insoluble disulphide,

$$C_6H_4Me{\cdot}S{\cdot}OH + HS{\cdot}C_6H_4Me = (C_6H_4MeS)_2 + H_2O,$$

whilst those derived from benzoic acid remain dissolved in the alkaline liquid.

In conclusion, we desire to express our thanks to Dr. J. A. Smythe for valuable criticism and to the Commissioners of the 1851 Exhibition for a grant which has enabled one of us to take part in this work.

KING'S COLLEGE, LONDON. [*Received, December 3rd,* 1923.]

XXIV.—*Tetrachloroiodides of Organic Bases.*

By FREDERICK DANIEL CHATTAWAY and FRANK LESLIE GARTON.

ONE of these comparatively little known salts was among the earliest iodine compounds to be investigated. Serullas (*Ann. Chim. Phys.*, 1829, **43**, 113) had examined the action of hydrochloric acid upon potassium iodate and had obtained what he regarded as a double salt of potassium chloride and acid potassium iodate. Filhol (*J. Pharm.*, 1839, **25**, 431, 506) repeated the work and showed that what Serullas had obtained was really a mixture; but on warming solid potassium iodate with slightly diluted hydrochloric acid at about 50° he found that a vigorous evolution of chlorine took place and that, on allowing the residue to cool, feathery, golden-yellow needles which proved to be potassium tetrachloroiodide separated. Filhol obtained the same compound more easily by passing chlorine into a strong solution of potassium iodide; iodine was first liberated but redissolved, yielding a golden-yellow liquid from which, on cooling, the characteristic needles of the tetrachloroiodide slowly separated. By the same method, Filhol also obtained the similar but more soluble ammonium salt.

If escape of chlorine is prevented, these compounds are remarkably stable and ammonium tetrachloroiodide may be kept in a sealed tube for years and even heated for many hours at 180—200° without any production of nitrogen chloride, nitrogen, or halogen acid (Chattaway, T., 1915, **107**, 105). The tetrachloroiodides have been little studied. Wells and various collaborators (*Z. anorg. Chem.*, 1892, **1**, 85; 1893, **2**, 255) prepared the tetrachloroiodides of cæsium, lithium, rubidium, and sodium, and shortly afterwards Weinland and Schlegelmilch (*ibid.*, 1902, **30**, 134) described a number of hydrated tetrachloroiodides of certain bivalent metals to which they assigned the general formula $M''Cl_2,2ICl_3,8H_2O$. Tetraethyl- and tetra-*n*-propyl-ammonium tetrachloroiodide (Chattaway and Hoyle, T., 1923, **123**, 661) and a few *N*-alkylpyridinium and quinolinium tetrachloroiodides have

been obtained in a pure state (Weltzien, *Annalen*, 1856, **99**, 1; Trowbridge and Diehl, *Amer. Chem. J.*, 1897, **19**, 558). Several authors have remarked the formation of yellow substances by the action of chlorine on the iodides of pyridine and quinoline, although the description of their properties and the analyses show that these products must have been very impure, if indeed they contained any tetrachloroiodide.

In the present paper, an account is given of a number of surprisingly stable tetrachloroiodides which are yielded by many very familiar organic bases, including urea, guanidine, pyridine, and quinoline.

These tetrachloroiodides can all be prepared by dissolving the corresponding base in concentrated hydrochloric acid, adding an equivalent of powdered iodine, and passing in excess of chlorine. The iodine gradually dissolves with considerable evolution of heat and the tetrachloroiodide either separates immediately or does so on allowing the resulting golden-yellow solution to cool in a slow current of chlorine. The yields are generally quantitative.

The organic tetrachloroiodides are all golden-yellow, crystalline compounds soluble in water, although with some decomposition. They may all be dissolved in a solution of iodine trichloride in hydrochloric acid. They can generally be recrystallised from a suitable solvent, although in some cases a little iodine trichloride must be added to prevent dissociation.

On heating, they appear to soften about 20° before melting. They melt, however, quite sharply, although in most cases with some decomposition. If heated above their melting points, they give off chlorine, iodine monochloride, and iodine, whilst a chloride of the base usually remains behind.

They are substances of remarkable stability, and many can be kept unaltered for a month or more in dry air or in a vacuum over lime.

There is very little evidence on which to base a general constitutional formula for these compounds. Ordinary valency formulæ in which the halogens are regarded as potentially tervalent assume linkings between them which appear somewhat fantastic.

It seems most in accordance with the properties of the tetrachloroiodides to assume that in them the iodine atom acts as the central atom of the negative ion, and that the four chlorine atoms are grouped tetrahedrally around it. The general formula thus becomes similar to that usually assigned to the chloroaurates :

$$\begin{bmatrix} Cl & Cl \\ & I \\ Cl & Cl \end{bmatrix} B \qquad \begin{bmatrix} Cl & Cl \\ & Au \\ Cl & Cl \end{bmatrix} K$$

EXPERIMENTAL.

Guanidine tetrachloroiodide, $NH{:}C(NH_2)\cdot NH_3ICl_4$, is easily soluble in a hot (70°) mixture of 5 parts of concentrated hydrochloric acid and 1 part of glacial acetic acid containing a little dissolved iodine trichloride. On cooling, it separates in clusters of bright golden-yellow, flattened prisms. By slow cooling, crystals 4 to 5 cm. long can easily be obtained. It melts at 163° (Found : Cl = 43·3; I = 38·45. $CH_6N_3Cl_4I$ requires Cl = 43·1; I = 38·60 per cent.). It is remarkably stable in dry air, and can be kept in a desiccator over lime for a long period; 0·7516 gram in one month lost only 0·0004 gram in weight, and on analysis showed a chlorine content of 43·2 per cent.

Carbamide tetrachloroiodide, $NH_2\cdot CO\cdot NH_3\cdot ICl_4,H_2O$, crystallises in long, slender, pale yellow needles inclined to twinning, m. p. 73° (Found : Cl = 40·9; I = 36·5. $CH_7O_2N_2Cl_4I$ requires Cl = 40·8; I = 36·5 per cent.). It is exceedingly easily soluble in water, giving a golden-yellow solution.

Pyridinium tetrachloroiodide, $C_5H_5N,HICl_4$.—Dittmar (*Ber.*, 1883, **18**, 1612) obtained pyridinium dichloroiodide by the action of a solution of iodine monochloride in hydrochloric acid on pyridine, and stated that he had obtained a more highly chlorinated product by passing chlorine over the dry dichloroiodide. His analyses and account of its properties show that his product was very impure. Trowbridge and Diehl (*loc. cit.*) passed chlorine into a solution of pyridinium hydriodide and probably obtained the tetrachloroiodide, but as they recrystallised it from alcohol, which decomposes it, they did not obtain it pure.

The tetrachloroiodides of pyridine, quinoline, etc., are so sparingly soluble that if the previously described method is employed they separate out before all the iodine has dissolved, and so interfere with the solution of the latter. A slightly different procedure has therefore to be adopted.

Fifteen grams of iodine were mixed with 200 c.c. of concentrated hydrochloric acid and chlorine was passed in until all the iodine had dissolved and no more chlorine was absorbed. To this solution was added, with constant stirring, a solution of 8 grams of pure pyridine in 20 c.c. of concentrated hydrochloric acid. A fine, chrome-yellow precipitate separated. After standing for half an hour, this was filtered off and recrystallised from acetic acid containing a few c.c. of a solution of iodine trichloride in hydrochloric acid. It can also be recrystallised from hydrochloric acid containing a little iodine trichloride, but in this it is much less easily soluble. It is best dried in a vacuum over lime or calcium chloride (Found :

Cl = 41·05; I = 36·1. $C_5H_6NCl_4I$ requires Cl = 40·7; I = 36·4 per cent.). Pyridinium tetrachloroiodide crystallises in slender, flattened prisms of a pale yellow colour which melt at 205° with decomposition.

α-Picolinium tetrachloroiodide, $C_5H_4MeN,HICl_4$, crystallises from a mixture of equal volumes of hydrochloric and acetic acids, in which it is moderately easily soluble, in irregularly-grown, flattened prisms of a bright yellow colour which show multiple twinning and melt with decomposition at 166° (Found : Cl = 39·0; I = 35·05. $C_6H_8NCl_4I$ requires Cl = 39·1; I = 35·0 per cent.).

Collidinium tetrachloroiodide, $C_5H_2Me_3N,HICl_4$, is very easily soluble in hot acetic acid, rather less easily soluble in hydrochloric acid, and crystallises from the latter in orange-yellow, long, flat, rhombic prisms twinned so as to appear like saw blades. It melts at 94° and decomposes with evolution of gas on further heating (Found : Cl = 36·12. $C_8H_{12}NICl_4$ requires Cl = 36·28 per cent.).

Quinolinium tetrachloroiodide, $C_9H_7N,HICl_4$, crystallises from acetic acid in clusters of long, slender, irregularly-grown prisms of a pale yellow colour which melt with decomposition at 195° (Found : Cl = 35·5; I = 31·9. $C_9H_8NCl_4I$ requires Cl = 35·5; I = 31·8 per cent.).

8-*Methylquinolinium tetrachloroiodide*, $C_9H_6MeN,HICl_4$, crystallises from a mixture of equal volumes of hydrochloric and acetic acids, in which it dissolves readily, in long, hair-like crystals of a pale yellow colour which melt at 152° with decomposition (Found : Cl = 34·46; I = 31·1. $C_{10}H_{10}NCl_4I$ requires Cl = 34·35; I = 30·7 per cent.).

6-*Nitroquinolinium tetrachloroiodide*, $NO_2{\cdot}C_9H_6N,HICl_4$, separates from a warm mixture of equal volumes of hydrochloric and acetic acids, in which it is sparingly soluble, in irregularly-grown, elongated plates of a dull yellow colour. It melts with decomposition at 131° (Found : Cl = 32·1; I = 28·85. $C_9H_7O_2N_2Cl_4I$ requires Cl = 32·0; I = 28·6 per cent.).

2-*Chloroquinolinium tetrachloroiodide*, $C_9H_6ClN,HICl_4$, crystallises from acetic acid in pale yellow, flattened prisms, m. p. 143° (decomp.) [Found : Cl (added) = 32·9; I = 29·2. $C_9H_7NCl_5I$ requires Cl (added) = 32·7; I = 29·3 per cent.].

6-*Chloroquinolinium tetrachloroiodide* separates from hydrochloric acid, in which it is sparingly soluble, as a dull yellow, crystalline powder, m. p. 131° (decomp.) [Found : Cl (added) = 33·05; I = 29·5. $C_9H_7NCl_5I$ requires Cl (added) = 32·7; I = 29·3 per cent.].

Quinaldinium tetrachloroiodide, $C_9H_6MeN,HICl_4$, crystallises from warm acetic acid, in which it is moderately easily soluble, in dull yellow, dendriform crystals, m. p. 149° (decomp.) (Found : Cl =

34·2; I = 30·8. $C_{10}H_{10}NCl_4I$ requires Cl = 34·35; I = 30·7 per cent.).

Caffeine tetrachloroiodide, $C_8H_{12}O_2N_4,HICl_4$, separates as a pale yellow, crystalline powder, m. p. 134° (decomp.) (Found: Cl = 30·1; I = 27·6. $C_8H_{13}O_2N_4Cl_4I$ requires Cl = 30·4; I = 27·2 per cent.).

Piperidinium tetrachloroiodide, $C_5H_{10}NH,HICl_4,H_2O$, exists in two polymorphic forms. It crystallises from acetic acid, in which it is readily soluble, in canary-yellow, fern-like crystals which on standing in contact with the mother-liquor for two days change completely into compact, six-sided prisms of an orange-yellow colour. Both forms melt with decomposition at 102° (Found: Cl = 38·1; I = 33·9. $C_5H_{14}ONCl_4I$ requires Cl = 38·0; I = 34·0 per cent.).

Piperazine bis-tetrachloroiodide, $HICl_4,NH<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>NH,HICl_4$, crystallises from hydrochloric acid, in which it is easily soluble, in bright yellow, compact prisms with domed ends (Found: Cl = 45·2; I = 40·8. $C_4H_{12}N_2Cl_8I_2$ requires Cl = 45·3; I = 40·6 per cent.). On heating, it darkens at temperatures above 100°; at 160°, iodine trichloride begins to sublime, and at 195° iodine is liberated, leaving a black, charred residue.

Pyridine-betaine tetrachloroiodide, $C_5H_5N(ICl_4)\cdot CH_2\cdot CO_2H$, crystallises from concentrated hydrochloric acid, in which it is moderately easily soluble, in bright yellow, compact, six-sided prisms, m. p. 133° (decomp.) (Found: Cl = 35·1; I = 31·2. $C_7H_8O_2NCl_4I$ requires Cl = 34·9; I = 31·2 per cent.).

Semicarbazide does not form a tetrachloroiodide, but is decomposed when treated with a solution of $HICl_4$. Nitrogen and carbon dioxide are evolved and on cooling ammonium tetrachloroiodide, NH_4ICl_4, separates.

Methylammonium tetrachloroiodide, $CH_3\cdot NH_2,HICl_4$, crystallises from hydrochloric acid, in which it is very easily soluble, in long, golden-yellow, hexagonal prisms with domed ends frequently twinned in star-shaped clusters. It melts with decomposition at 96° (Found: Cl = 46·9; I = 42·3. CH_6NCl_4I requires Cl = 47·15; I = 42·2 per cent.).

Dimethylammonium tetrachloroiodide, $(CH_3)_2NH,HICl_4$, is easily soluble in warm hydrochloric acid, from which it crystallises in compact, orange-yellow prisms, m. p. 82° (decomp.) (Found: Cl = 44·9; I = 40·5. $C_2H_8NCl_4I$ requires Cl = 45·05; I = 40·3 per cent.).

Trimethylammonium tetrachloroiodide, $(CH_3)_3N,HICl_4$, crystallises from warm hydrochloric acid, in which it is sparingly soluble, in

canary-yellow plates, m. p. 182° (decomp.) (Found: Cl = 43·30; I = 38·65. $C_3H_{10}NCl_4I$ requires Cl = 43·39; I = 38·83 per cent.).

Ethylammonium tetrachloroiodide, $C_2H_5{\cdot}NH_2,HICl_4$, is very easily soluble in acetic acid, rather less soluble in hydrochloric acid. From the latter solvent it crystallises in very hygroscopic, orange-yellow, compact rhombs, m. p. 45° (Found: Cl = 44·7; I = 39·9. $C_2H_8NCl_4I$ requires Cl = 45·05; I = 40·3 per cent.).

Diethylammonium tetrachloroiodide, $(C_2H_5)_2NH,HICl_4$, crystallises from warm hydrochloric acid, in which it is moderately easily soluble, in thin, four-sided plates of a pale yellow colour melting with decomposition at 79° (Found: Cl = 41·4; I = 36·8. $C_4H_{12}NCl_4I$ requires Cl = 41·5; I = 37·1 per cent.).

Ethylenediammonium bis-tetrachloroiodide, $\left.\begin{matrix}CH_2{\cdot}NH_2,HICl_4\\ CH_2{\cdot}NH_2,HICl_4\end{matrix}\right\}2H_2O$, crystallises from hydrochloric acid, in which it is sparingly soluble, in golden-yellow, long, hexagonal prisms, m. p. 105° (decomp.) (Found: Cl = 44·7; I = 40·0. $C_2H_{14}O_2N_2Cl_8I_2$ requires Cl = 44·6; I = 39·9 per cent.).

Benzylammonium tetrachloroiodide, $C_6H_5{\cdot}CH_2{\cdot}NH_2,HICl_4$, crystallises from acetic acid, in which it is readily soluble, in flattened, yellow prisms, m. p. 97° (decomp.) (Found: Cl = 37·6. $C_7H_{10}NCl_4I$ requires Cl = 37·6 per cent.).

Dibenzylammonium tetrachloroiodide, $(C_6H_5{\cdot}CH_2)_2NH,HICl_4$, crystallises from acetic acid, in which it is moderately easily soluble, in fine, yellow needles, m. p. 165° (Found: Cl = 29·9; I = 27·2. $C_{14}H_{16}NCl_4I$ requires Cl = 30·4; I = 27·2 per cent.).

Tribenzylammonium tetrachloroiodide, $(C_6H_5{\cdot}CH_2)_3N,HICl_4$, crystallises from acetic acid, in which it is sparingly soluble, in yellow rhombs, m. p. 100° (decomp.) (Found: Cl = 25·85; I = 22·7. $C_{21}H_{22}NCl_4I$ requires Cl = 25·46; I = 22·8 per cent.).

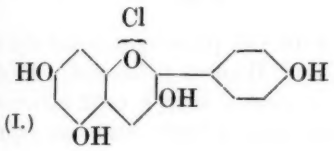
THE QUEEN'S COLLEGE, OXFORD. [*Received, November 12th*, 1923.]

XXV.—*A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part III. A New Synthesis of Pelargonidin Chloride.*

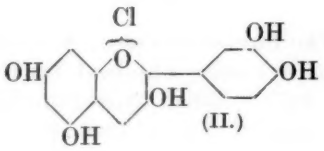
By DAVID DOIG PRATT and ROBERT ROBINSON.

A PROMISING feature of the method of preparation of anthocyanidin salts, which it is the object of this series of investigations to develop, resides in its applicability to the synthesis of the whole range of the naturally occurring anthocyanidins, including those containing both hydroxyl and methoxyl groups. The investigations of Willstätter

and his collaborators have demonstrated that the anthocyanin pigments yield on hydrolysis various carbohydrates, occasionally an acidic fragment, and up to the present only three fundamental anthocyanidins, namely, pelargonidin (I), cyanidin (II), and delphinidin (III), formulated as chlorides.



(I.)



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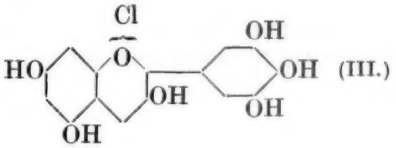
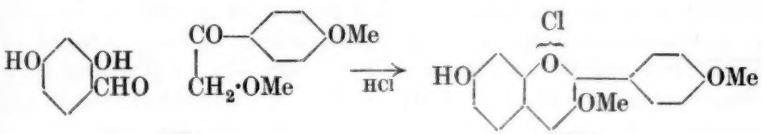


(III.)

Several methyl and dimethyl ethers of delphinidin and a methyl ether of cyanidin have, however, been obtained, and it is perhaps in connexion with these substances that constitutional evidence derived from synthetical experiments will prove to be of the greatest value. Before proceeding to this more difficult step, we have, in the first place, directed our attention to the comparatively simple case of pelargonidin, chiefly because the required ketonic component, namely, ω : 4-dimethoxyacetophenone (IV), has already been prepared in a pure condition (Part II, T., 1923, **123**, 750) and found to condense with particular facility with β-resorcylaldehyde in glacial acetic acid solution by the agency of hydrogen chloride. The reaction proceeds in accordance with the scheme :

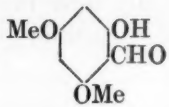


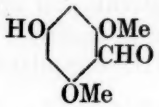
(IV.) (V.)

In order to obtain pelargonidin chloride di-, tri-, or tetra-methyl ether, it is obvious that the resorcylaldehyde must be replaced by phloroglucinaldehyde or one of its derivatives, and we have obtained the best results with the methyl ethers.

Dimroth and Zoeppritz (*Ber.*, 1902, **35**, 995) prepared resorcylaldehyde by hydrolysis of the product of condensation of resorcinol and formanilide under the influence of phosphoryl chloride, and applying a similar method to phloroglucinol dimethyl ether we have found that 2-hydroxy-4 : 6-dimethoxybenzaldehyde (VI) and a

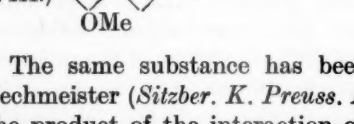
smaller relative amount of 4-hydroxy-2 : 6-dimethoxybenzaldehyde (VII) are produced.

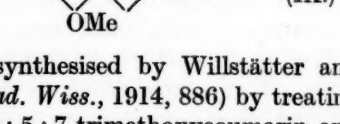
(VI.) 



(VII.)

The former substance is identical with the phloroglucinaldehyde dimethyl ether obtained by Herzig and Wenzel (*Monatsh.*, 1903, **24**, 857). When hydrogen chloride is passed into a cold ethereal solution of 2-hydroxy-4 : 6-dimethoxybenzaldehyde and an equimolecular proportion of ω : 4-dimethoxyacetophenone, a good yield of tetramethylpelargonidin chloride (VIII) is obtained and most of the substance separates from the solution in a fine crystalline condition.

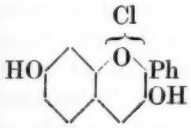
(VIII.) 



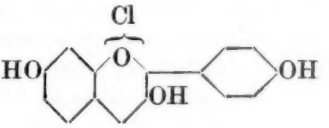
(IX.)

The same substance has been synthesised by Willstätter and Zechmeister (*Sitzber. K. Preuss. Akad. Wiss.*, 1914, 886) by treating the product of the interaction of 3 : 5 : 7-trimethoxycoumarin and magnesium anisyl bromide with hydrochloric acid, but analyses have not previously been recorded. The salt crystallises with $2{\cdot}5H_2O$, and the corresponding *ferrichloride* separates from acetic acid in an anhydrous condition. The tetramethyl ether was demethylated by following the method adopted by Willstätter and Zechmeister (*loc. cit.*), and the pelargonidin chloride (I) finally obtained exhibited all the numerous recorded properties (p. 199) of the compound obtained from the scarlet pelargonium as fully detailed by Willstätter and Bolton (*Annalen*, 1915, **408**, 42). 4-Hydroxy-2 : 6-dimethoxybenzaldehyde (VII) yields a trimethylpelargonidin chloride (IX) when it is condensed in ethereal solution with ω : 4-dimethoxyacetophenone by means of hydrogen chloride. The reaction is curious in that it involves elimination of a methyl group in the course of the formation of the pyrylium nucleus. The same salt was obtained by a similar method from 2 : 4-dihydroxy-6-methoxybenzaldehyde, itself produced by application of the formanilide process to phloroglucinol monomethyl ether. This trimethylpelargonidin chloride closely resembles the tetramethyl ether in most respects, but it is characterised by much more sparing solubility in dilute hydrochloric acid and by the formation of a relatively stable violet colour-base. The condensation of phloroglucinaldehyde

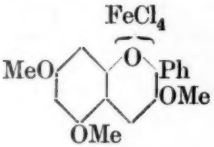
and ω : 4-dimethoxyacetophenone has also been carried out, but further investigation of the conditions of production of dimethylpelargonidin derivatives is necessary. In connexion with the interpretation of the colour reactions of the anthocyanidins we have examined 3 : 7-dihydroxy- and 3 : 4′ : 7-trihydroxy-2-phenylbenzopyrylium chlorides (X, XI), prepared by dealkylation of salts



(X.)



(XI.)



(XII.)

previously described. The substance (XI), in spite of its close constitutional relationship to pelargonidin, gives an intense reddish-purple coloration in aqueous solution on the addition of sodium carbonate. The pure blue coloration characteristic of pelargonidin and other anthocyanidins is probably dependent on the presence of at least four hydroxyl groups in the molecule as well as on their positions. It is evident also that hydroxyls in positions 3 and 4′ have a very considerable deepening effect on the colour reaction with sodium carbonate. In the case of the hydroxyl in position 4′, this follows from a comparison of (X) and (XI) and of acacetidin and apigenidin chlorides,* and in the case of hydroxyl in position 3 from a comparison of (XI) with apigenidin. The above remarks apply only to the hydroxyflavylium salts. 3 : 5 : 7-Trimethoxy-2-phenylbenzopyrylium ferrichloride (XII) has been prepared by condensation of 2-hydroxy-4 : 6-dimethoxybenzaldehyde and ω-methoxyacetophenone by means of hydrogen chloride in ethereal solution, followed by treatment of the product with ferric chloride. It is related to the flavonol *galangin*, and attempts are being made to obtain the demethylated compounds, which may be termed *galangidin* salts.

Experimental.

3 : 7-*Dihydroxy*-2-*phenylbenzopyrylium Chloride* (Formula X).—7-Hydroxy-3-ethoxy-2-phenylbenzopyrylium chloride (Part I, T., 1922, **121**, 1582) (5 grams) and phenol (9 grams) were added to hydriodic acid (60 c.c.; *d* 1·7) and the mixture was gently boiled during thirty minutes in a stream of carbon dioxide. On cooling, no separation of the iodide occurred, and the product was isolated

* Acacetidin chloride is described in Part IV (p. 204). Apigenidin chloride and luteolidin chloride will be described subsequently; the former gives a bright damson solution and the latter a bluish-violet solution in aqueous sodium carbonate.

by the successive addition of water (60 c.c.) and ether (120 c.c.). Glistening, yellowish-red platelets crystallised on standing, and these were collected, washed with ether, and dried in the air (3·5 grams). This iodide was converted into the chloride by treatment during fifteen minutes with an excess of precipitated silver chloride in boiling dilute hydrochloric acid (30 c.c.). The filtered solution, on cooling, deposited orange-brown, rhombic prisms, which were collected and dried over sulphuric acid in a vacuum (Found: C = 61·7; H = 4·4. $C_{15}H_{11}O_3Cl,H_2O$ requires C = 61·6; H = 4·4 per cent.). On heating, this salt darkens at 110° and decomposes at 184°. It dissolves in methyl, ethyl, and *iso*amyl alcohols to yellow solutions which exhibit a weak green fluorescence. Its yellow solution in concentrated sulphuric acid exhibits a green fluorescence much deeper in tone than that of pelargonidin chloride or 3 : 7 : 4′-trihydroxy-2-phenylbenzopyrylium chloride under similar conditions. Addition of sodium acetate to an amyl-alcoholic solution produces a red colour which soon fades and with aqueous sodium carbonate the alcoholic layer is coloured violet. When sodium acetate is added to an aqueous acid solution, the red colour base is precipitated. The salt is soluble in tap-water to a reddish-violet solution, which becomes pale violet on the addition of a trace of acetic acid; the liquid then contains the pseudo-base and the addition of mineral acid restores the yellow colour of the oxonium salt. This salt reduces Fehling's solution only to a small extent on warming.

3 : 7 : 4′-*Trihydroxy-2-phenylbenzopyrylium Chloride* (Formula XI).—A mixture of 7-hydroxy-3 : 4′-dimethoxy-2-phenylbenzopyrylium chloride (Part II; T., 1923, **123**, 751) (4·5 grams), hydriodic acid (100 c.c.; *d* 1·7), and phenol (13 grams) was boiled moderately vigorously during thirty minutes in a current of carbon dioxide. On cooling, the demethylated iodide separated in clusters of yellowish-brown, frond-like needles, which were collected, washed with light petroleum and then ether, and dried in the air (2·6 grams). After conversion into the chloride by means of silver chloride and hot dilute hydrochloric acid, the salt was precipitated from the filtrate by means of concentrated hydrochloric acid and recrystallised from hot dilute hydrochloric acid. It separated in aggregates of glistening, prismatic needles having a purple reflex and was collected and dried in a vacuum over sulphuric acid (Found: C = 58·2; H = 4·4. $C_{15}H_{11}O_4Cl,H_2O$ requires C = 58·4; H = 4·2 per cent.). On heating, the substance turns green at about 200°, sinters at 250°, and decomposes at 262°. It is insoluble in chloroform, but dissolves in the simple alcohols to yellow solutions which exhibit green fluorescence. The yellowish-green fluorescence of the solution in

sulphuric acid is brilliant. The yellowish-red solution in dilute hydrochloric acid is completely extracted on shaking with *iso*amyl alcohol. This alcoholic layer becomes red on the addition of sodium acetate and the colour fades on standing owing to formation of the pseudo-base, whilst the addition of aqueous sodium carbonate produces a fine pure blue coloration in the alcoholic layer and a red, aqueous layer. The reaction with sodium acetate is similar in aqueous solution, but in this case sodium carbonate gives a stable reddish-purple colour. Dilute ferric chloride gives no characteristic reaction. The salt reduces Fehling's solution on warming. When treated with an excess of tap-water, a purple solution of the colour-base is produced, and on the addition of a trace of acetic acid the liquid is slowly decolorised in the cold and then contains the pseudo-base. The solution in distilled water is orange-red and also becomes colourless on heating. These solutions of the pseudo-base become orange on the addition of hydrochloric acid as the result of formation of the oxonium salt.

Dimethyl Ethers of Phloroglucinol and Phloroglucinaldehyde.—Phloroglucinol dimethyl ether has been prepared by the following modification of Weidel and Pollak's method (*Monatsh.*, 1900, **21**, 22). Anhydrous phloroglucinol (25 grams) was dissolved in dry acetone-free methyl alcohol (150 c.c.) and a stream of hydrogen chloride passed through the solution during an hour at such a rate as to raise the solvent to the boiling point. The liquid was then boiled under reflux during an hour and after once more saturating with hydrochloric acid for one further hour was allowed to remain over-night. The greater part of the methyl alcohol was removed by distillation, the heavy oil precipitated on the addition of water was taken up in ether, and the ethereal solution washed with water, dried with sodium sulphate, and distilled. There resulted 20 grams of phloroglucinol dimethyl ether, b. p. 198—200°/35 mm., and 3·5 grams of phloroglucinol monomethyl ether, b. p. 220°/35 mm. Very similar results in point of yield were obtained by saturating the methyl-alcoholic solution of phloroglucinol with hydrogen chloride in the cold and allowing to remain during twelve days. Undoubtedly the most satisfactory method of introduction of the formyl group into the nucleus of polyhydric phenols is by the Gattermann synthesis, but in the early stages of this investigation the conditions were such that the employment of a process involving the manipulation of anhydrous hydrocyanic acid was not deemed prudent, and we had recourse to the alternative method of Dimroth and Zoeppritz (*loc. cit.*), which, however, gave only moderately satisfactory results in the particular application which we wished to make. A mixture of phloroglucinol dimethyl ether (22 grams),

formanilide (17·4 grams), anhydrous ether (150 c.c.), and phosphoryl chloride (7·4 grams) was gently heated on the steam-bath and after half an hour a heavy oil began to separate from the dark red liquid. After one and a half hours from the commencement, the heating was discontinued and the containing vessel corked and allowed to remain during twenty-four hours. The ether was decanted from the hard solid mass of condensation product and the latter broken up and thoroughly washed with fresh ether. This substance is essentially a salt of the composition $(MeO)_2C_6H_2(OH)\cdot CH{:}NPh,HCl$, and was hydrolysed by repeated and prolonged mechanical shaking with water (500 c.c. for each 5 grams of the salt) and a large volume of ether. After a few hours, the ethereal layer was separated and fresh ether added, and if the aqueous solution was not acid to congo this was secured by the addition of just sufficient hydrochloric acid. The combined ethereal extracts were washed with dilute hydrochloric acid in order to remove any free Schiff base, dried with sodium sulphate, and after removal of the solvent the residue was distilled under diminished pressure. Ten grams of a pale yellow oil, b. p. 190—195°/25 mm., were obtained. This crystallised on keeping and after recrystallisation from aqueous methyl alcohol was obtained in needles melting at 70°. The substance is identical with 2-hydroxy-4 : 6-dimethoxybenzaldehyde, m. p. 70°, obtained by Herzig and Wenzel by hydrolysis of the imine hydrochloride derived from the condensation of phloroglucinol dimethyl ether and hydrocyanic acid in presence of hydrogen chloride. In some cases, the crude aldehyde was not immediately distilled and it was then observed partly to crystallise on standing. The solid was examined and found to consist of a new substance which is sparingly soluble in benzene, and this is evidently destroyed in the process of distillation. The whole product was dissolved in hot benzene, and the crystals which separated on cooling were recrystallised from the same solvent. The colourless, rectangular prisms melt at 190° with some darkening above 180° (Found: C = 59·4; H = 5·1. $C_9H_{10}O_4$ requires C = 59·4; H = 5·5 per cent.). This compound is not identical with 2 : 4-dihydroxy-6-methoxybenzaldehyde, but equally with the latter yields trimethylpelargonidin chloride on condensation with ω : 4-dimethoxyacetophenone in presence of hydrogen chloride, and from these observations in conjunction with the analytical results it is evident that the substance must be 4-hydroxy-2 : 6-dimethoxybenzaldehyde (VII).

The formanilide process has also been applied to the preparation of 2 : 4-dihydroxy-6-methoxybenzaldehyde (compare Herzig and Wenzel, *loc. cit.*), and in this case with satisfactory results. The proportions of starting materials employed were phloroglucinol

monomethyl ether (6·0 grams), formanilide (5·2 grams), phosphoryl chloride (2·2 grams), ether (50 c.c.), and the details of the process were similar to those described above, except that the product (4·0 grams) was purified by crystallisation. The method is, however, unsuitable for the preparation of phloroglucinaldehyde, the difficulty occurring at the stage of hydrolysis of the Schiff base. 2·5 Grams of the aldehyde were obtained from 9 grams of phloroglucinol. Latterly, in view of the superior yields, we have returned to the Gattermann synthesis, and have adopted the following device in order to minimise the inconvenience arising from the habitual use of anhydrous hydrocyanic acid. The gas is generated from a known weight of potassium cyanide by adding 70 per cent. sulphuric acid from a tap-funnel and in a flask through which a current of carbon dioxide can be passed. The mixed gases are subsequently dried by means of U-tubes containing calcium chloride. An ethereal solution of phloroglucinol dimethyl ether (for example) is contained in a flask closed by a cork bearing two wide delivery tubes and a condenser. Dry hydrogen chloride and the diluted hydrocyanic acid are passed alternately into the solution and when all the potassium cyanide has been decomposed the liquid is thoroughly saturated with hydrogen chloride. On standing, the imine hydrochloride separates out and after decomposition with water in the usual manner an excellent yield of pure phloroglucinaldehyde dimethyl ether is obtained.

Trimethylgalangidin Ferrichloride (Formula XII).—A rapid stream of dry hydrogen chloride was passed into a solution of 2-hydroxy-4 : 6-dimethoxybenzaldehyde (2·4 grams) and ω-methoxyacetophenone (2·0 grams) in anhydrous ether (25 c.c.), when the solution at once became red and after an hour deep crimson. The current of gas was stopped after two hours and crystallisation of the product induced by cooling and scratching the sides of the containing vessel. After allowing to remain in a cool place overnight, slender, glistening needles filled the liquid, and these were collected, washed with ether, and dried in the air (1·2 grams). A further quantity was recovered from the mother-liquor by washing with dilute hydrochloric acid, followed by conversion into the ferrichloride (0·4 gram). *Trimethylgalangidin chloride* crystallises from dilute hydrochloric acid in balls of slender, orange-red needles. The *ferrichloride* crystallises from acetic acid in yellowish-brown, rectangular prisms melting at 174° without obvious decomposition (Found : C = 43·8; H = 3·2. $C_{18}H_{17}O_4Cl_4Fe$ requires C = 42·7; H = 3·4 per cent.).

This derivative is soluble in chloroform to a red solution, and in sulphuric acid to a yellow solution which exhibits apple-green

fluorescence. It is soluble to a reddish-violet solution in hot dilute hydrochloric acid, but it is sparingly soluble in cold alcohol. On heating, an orange liquid results, and this becomes reddish-violet on the addition of hydrochloric acid. Solutions of trimethylgalangidin salts are decolorised by the addition of sodium acetate or sodium carbonate, and the colour is restored by acidification.

7-Hydroxy-3 : 5 : 4′-trimethoxy-2-phenylbenzopyrylium Chloride (Trimethylpelargonidin Chloride) (Formula IX).—A moderately rapid stream of hydrogen chloride was passed through a solution of 2 : 4-dihydroxy-6-methoxybenzaldehyde (4·0 grams) and ω : 4-dimethoxyacetophenone (4·5 grams) in dry ether (75 c.c.) during two hours. The deep crimson solution was allowed to remain overnight in the vicinity of crushed potassium hydroxide so as to assist in diminishing the concentration of hydrogen chloride in the solution, a condition which was found to assist crystallisation. A certain proportion of the product crystallised and was collected and a further quantity was isolated by the addition of alcohol and a little water. Finally the whole mother-liquor was boiled with dilute hydrochloric acid so as to remove the organic solvents.

The filtered solution deposited moderately pure material and the total yield was 2·0 grams. This salt crystallises well from hot dilute hydrochloric acid, in which it is sparingly soluble, in long, prismatic needles, reddish-violet in mass, but yellowish-brown by transmitted light under the microscope, and exhibiting a fine green glance (Found: in material dried over sulphuric acid in a vacuum, C = 55·5; H = 6·2; loss at 105° in high vacuum = 12·2; in anhydrous material, C = 62·2; H = 5·0. $C_{18}H_{17}O_5Cl$, $2{\cdot}5H_2O$ requires C = 55·0; H = 5·9; H_2O = 11·5. $C_{18}H_{17}O_5Cl$ requires C = 62·1; H = 4·9 per cent.). The anhydrous salt is very hygroscopic and melts at 130°. It is readily soluble in the simple alcohols to orange-red solutions with a blue tinge and in chloroform to a red solution. The fluorescence in sulphuric acid is bright apple-green. On the addition of tap-water to the salt itself or its alcoholic solution, a beautiful violet solution of the colour-base is obtained and the latter is deposited on standing. Distilled water gives a pink solution on warming, and this contains the pseudo-base, but if the reagent be added slowly the result is complete decolorisation owing to formation of the pseudo-base. An aqueous solution of the chloride is completely extracted by *iso*amyl alcohol, which is coloured red, and violet on the subsequent addition of sodium acetate.

This salt was also obtained when hydrogen chloride was passed into an ice-cold solution of 4-hydroxy-2 : 6-dimethoxybenzaldehyde (0·5 gram) and ω : 4-dimethoxyacetophenone (0·5 gram) in ether (10 c.c.). In the course of two hours the characteristic metallic-

looking crystals of the chloride began to separate and when the crystallisation was completed the substance was collected (0·2 gram), washed with ether, and recrystallised from dilute hydrochloric acid. In every respect, the substance was found to be identical with the trimethylpelargonidin chloride described above. The *ferrichloride* crystallises from glacial acetic acid in brown, compact, rectangular, microscopic prisms melting at 168°. It may be mentioned here that attempts have been made to condense phloroglucinaldehyde with ω : 4-dimethoxyacetophenone by means of hydrogen chloride in ethereal solution. The chloride which separated from the solution could not be satisfactorily purified, but the ethereal mother-liquor. on washing with water and treatment of the aqueous extract with ferric chloride and hydrochloric acid, yielded a *ferrichloride* which gave the reactions to be expected in the case of a dimethylpelargonidin salt. This derivative crystallises from acetic acid in long, slender needles or from formic acid in prismatic needles and darkens at 180°, but does not melt under 330°. Its pink solution in concentrated sulphuric acid exhibits bright apple-green fluorescence. It is soluble in alcohol or chloroform to red solutions with a violet tinge. Whilst almost insoluble in dilute hydrochloric acid in the cold, it dissolves on warming to an orange-red liquid which becomes bordeaux-red on the addition of sodium acetate, the colour disappearing on standing. The use of phloroglucinaldehyde in these syntheses is being further investigated.

3 : 5 : 7 : 4′-*Tetramethoxy*-2-*phenylbenzopyrylium Chloride* (*Tetramethylpelargonidin Chloride*) (Formula VIII).—When a moderately rapid stream of hydrogen chloride was led into a solution of freshly distilled 2-hydroxy-4 : 6-dimethoxybenzaldehyde (5·0 grams) and ω : 4-dimethoxyacetophenone (5·2 grams) in anhydrous ether (30 c.c.) the liquid quickly became red and then deep crimson. After about an hour, crystallisation of the product was induced by cooling and scratching, the passage of the gas continued during a further hour, and the mixture then allowed to remain over-night. The glistening crystals had a fine green reflex and almost filled the liquid. Under the microscope, they were seen to consist of slender needles which quickly changed on the slide to much more compact, prismatic needles. The substance was collected, washed with ether, and dried in the air (4·0 grams). A further quantity (1·0 gram) was recovered from the mother-liquor in the form of ferrichloride. The chloride crystallises from dilute hydrochloric acid in prisms which are yellowish-brown by transmitted light under the microscope and have a characteristic dark medial band. In mass they exhibit a beautiful golden-green sheen, whilst a crystalline film deposited on a glass surface is reddish-violet by transmitted light (Found : in

material dried over sulphuric acid in a vacuum, C = 56·2; H = 6·3; in material dried at 105° in a high vacuum, C = 63·1; H = 5·1. $C_{19}H_{19}O_5Cl$, $2{\cdot}5H_2O$ requires C = 56·0; H = 5·9. $C_{19}H_{19}O_5Cl$ requires C = 63·0; H = 5·2 per cent.).

The salt loses its lustre at 100° and melts at 143°; it is hygroscopic when anhydrous. The substance is readily soluble in alcohol to an orange-red solution, which is immediately decolorised by the addition of tap-water, sodium acetate, or sodium carbonate. The red colour of the oxonium salts is restored by the addition of hydrochloric acid. It is sparingly soluble in cold chloroform, and more readily soluble in the hot solvent to a pink solution. The red solution in concentrated sulphuric acid exhibits dull green fluorescence. Whilst the substance is very readily soluble in hot dilute hydrochloric acid, the separation on cooling is almost complete. In tap-water, an orange-red solution is momentarily obtained; this becomes pale violet and on warming colourless. In distilled water, a pink solution results; this is not decolorised on heating, but the colour is discharged on the addition of a few drops of tap-water. The chloride is completely extracted from an aqueous solution by *iso*amyl alcohol, the latter acquiring a red colour which is at once discharged by the addition of sodium acetate. If a little of the chloride be covered with pyridine, a purple solution is obtained and this quickly becomes yellowish-brown. On heating, the reddish-purple colour is again observed and this changes back to yellowish-brown on cooling.

Ferrichloride.—This derivative, obtained in the usual manner, separates from hot acetic acid in orange-red, rectangular prisms. It is, however, sparingly soluble in this solvent and is more conveniently crystallised from formic acid, being thus obtained in clusters of needles which darken at 190° and melt at 204° (Found: C = 43·6; H = 3·8. $C_{19}H_{19}O_5Cl_4Fe$ requires C = 43·6; H = 3·6 per cent.). The substance is soluble in alcohol to a red solution and in chloroform to a reddish-violet solution.

Pelargonidin Chloride (Formula I).—The demethylation of tetramethylpelargonidin chloride, prepared by the method recorded in the preceding section, was carried out in the manner described by Willstätter and Zechmeister (*loc. cit.*) in the case of the salt derived from the product of the condensation of trimethoxycoumarin and magnesium anisyl bromide. The crude pelargonidin chloride was crystallised from 4 per cent. aqueous hydrochloric acid and dried in a vacuum over sulphuric acid (Found: C = 56·0; H = 4·4. $C_{15}H_{11}O_5Cl,H_2O$ requires C = 55·6; H = 4·0 per cent.). The crystals were dark brownish-violet, rectangular prisms, which did not melt under 350° and were soluble in methyl and ethyl alcohols to red solutions with a violet tinge. An aqueous acid solution is

completely extracted on shaking with *iso*amyl alcohol and on the addition of sodium acetate the colour changes to violet and remains in the alcoholic layer. On the addition of sodium carbonate, however, to the *iso*amyl alcohol solution, a fine pure blue colour is produced and passes completely to the aqueous layer. Lead acetate gives a blue precipitate when added to an alcoholic solution and the salt reduces Fehling's solution on warming. It dissolves in distilled water to a red solution which is decolorised on heating owing to the formation of the pseudo-base. The crude compound is often mixed with an impurity which crystallises in slender needles, and the absorption spectrum was examined in the case of a specimen which was recrystallised until found to be perfectly homogeneous when inspected microscopically. As the observation was visual, the conditions were adjusted so that the position of the absorption band of cyanidin chloride could be correctly estimated. The synthetical pelargonidin chloride was then found to show two bands in the positions assigned by Willstätter and Bolton (*loc. cit.*) to those exhibited by the salt derived from natural sources.

0·008 *Gram in* 56 *c.c. of ethyl alcohol containing a trace of hydrogen chloride.*

Thickness.	Band.	Synthetical.	W. and B.*
2·5 mm.	I	577···569—489···480	579···569—491···483
,,	II	450···not sharp	448···442
5 mm.	I	583···574—474	588···576—471
,,	II	446—	448—

* 0·007 Gram in 50 c.c. of ethyl alcohol.

One of us (D. D. P.) desires to thank the Carnegie Trust for a scholarship which has enabled him to take part in this investigation.

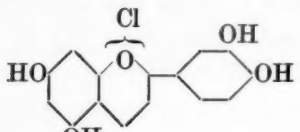
UNIVERSITIES OF ST. ANDREWS AND MANCHESTER. [*Received, November 26th,* 1923.]

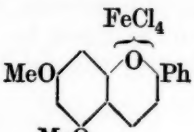
XXVI.—*A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part IV. Flavylium Salts Related to Chrysin, Apigenin, and Luteolin.*

By DAVID DOIG PRATT, ROBERT ROBINSON, and PERCY NOEL WILLIAMS.

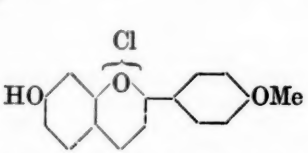
ALTHOUGH the greater interest attaches to the flavylium salts related to the naturally occurring flavonols, the wide distribution of the flavones suggests that certain of the corresponding pyrylium salts may ultimately be derived by hydrolysis of plant pigments.

Thus in the series containing phloroglucinol and catechol nuclei connected by a three-carbon chain the most highly oxidised member is the flavonol quercetin; next come cyanidin chloride and luteolin, which have the same state of oxidation. More reduced is hyssopinglycone (Oesterle, *Schweiz. Apoth. Ztg.*, 1921, **59**, 548; 1922, **60**, 441; compare *Annual Reports*, 1922, 120), and the final reduction product is possibly represented by catechin. It would be strange indeed if the flavylium salt analogous to luteolin should prove to be almost the only missing member of the group. For this reason, we propose to attempt the preparation and characterisation of a series of these compounds, which may conveniently be designated by names suggesting their relationship to particular flavones and having the termination *-idin*. Thus the compound (I) is luteolidin chloride, and experiments on the synthesis of this substance are in progress, whilst a derivative is briefly described below.

(I.) 



(II.)



(III.)

The dimethyl ether of chrysinidin * chloride results when hydrogen chloride is passed into an acetic acid solution of 2-hydroxy-4 : 6-dimethoxybenzaldehyde (Part III, this vol., p. 194) and acetophenone. The substance was isolated as the ferrichloride (II), which is a characteristic derivative.

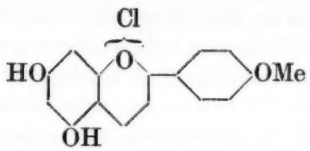
p-Anisyl β-hydroxyvinyl ketone, the copper salt of which was analysed, condenses with resorcinol under the influence of hydrogen chloride to form the oxonium chloride (III), which may, however, be more conveniently prepared from β-resorcylaldehyde and *p*-acetylanisole.

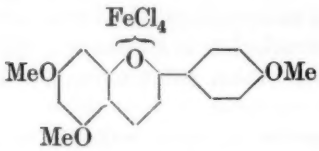
With phloroglucinol in ethereal solution, the hydroxy-ketone reacts in presence of hydrogen chloride to form acacetidin † chloride (IV). This very sparingly soluble salt was ultimately obtained by crystallisation from a large volume of ethyl alcohol

* The expression "chrysidin" is inadmissible, as it has already been used to denote certain naphthacridines.

† The flavone acacetin derived from *Robinia pseudacacia* (Linn.) has been shown by A. G. Perkin (T., 1900, **71**, 430) to be an apigenin methyl ether very probably identical with the substance obtained by von Gerichten from apigenin (*Ber.*, 1900, **33**, 2908) and from which anisic acid may be derived.

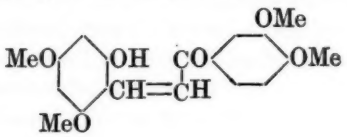
containing hydrochloric acid in beautiful reddish-brown, anhydrous prisms having a beetle-green lustre.

(IV.) 

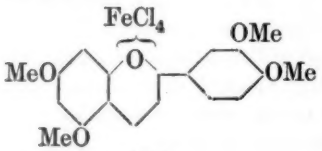


(V.)

Trimethylapigenidin ferrichloride (V) has also been prepared from 2-hydroxy-4 : 6-dimethoxybenzaldehyde and acetylanisole by condensation in presence of methyl-alcoholic potassium hydroxide, followed by treatment of the potassium salt of the resulting unsaturated ketone with hot concentrated hydrochloric acid and subsequently with ferric chloride. Attempts to condense 2-hydroxy-4 : 6-dimethoxybenzaldehyde and acetoveratrone by means of hydrogen chloride did not give satisfactory results. In presence of potassium hydroxide, however, 2-hydroxy-4 : 6-dimethoxystyryl 3 : 4-dimethoxyphenyl ketone (VI) was obtained in the normal manner and this derivative of salicylideneacetophenone was found to be very readily and completely changed to tetramethyl-luteolidin salts by the action of acids. The ferrichloride (VII) is well adapted for the characterisation of this series of salts.



(VI.)



(VII.)

EXPERIMENTAL.

Dimethylchrysinidin Ferrichloride (Formula II).—A moderate stream of hydrogen chloride was passed during two hours through a solution of 2-hydroxy-4 : 6-dimethoxybenzaldehyde (1·5 grams) and acetophenone (1·4 grams) in glacial acetic acid (10 c.c.). The liquid quickly assumed an intense orange-red colour, but no crystalline chloride separated. Water was added and the solution filtered to remove a little oily matter, after which a brick-red ferrichloride was precipitated by the addition of a large excess of ferric chloride dissolved in concentrated hydrochloric acid. The substance was collected and crystallised from acetic acid, in which it is sparingly soluble in the cold. The glistening, reddish-brown prisms which separated were shaped like the leaf of a palm but with curiously jagged edges, and melted at 178° after softening at 175—176° (Found : C = 43·8; H = 3·4. $C_{17}H_{15}O_3Cl_4Fe$ requires C = 43·9;

H = 3·2 per cent.). This derivative is readily soluble in water to a yellowish-orange solution and moderately soluble in chloroform. It crystallises from the latter solvent in jagged prisms. Its bright yellow solution in sulphuric acid exhibits green fluorescence, which becomes more intense on standing. Addition of sodium acetate to an aqueous solution produces a milky suspension of a colourless pseudo-base, which may be removed by extraction with ether and subsequently reconverted into the ferrichloride melting at 178°. The condensation described above did not proceed satisfactorily in ethereal solution.

p-*Anisyl* β-*Hydroxyvinyl Ketone*, $OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CH{:}CH{\cdot}OH$.—*p*-Acetylanisole was obtained by a slight modification of the method of Charon and Zamonos (*Compt. rend.*, 1901, **133**, 742). Acetyl chloride (25 grams) was slowly added to a cold mixture of anisole (20 grams), carbon disulphide (150 c.c.), and powdered anhydrous aluminium chloride (35 grams). The flask was frequently shaken during one hour and the reaction completed by gently warming on the steam-bath. The product was isolated in the usual manner and distilled (b. p. 260°, m. p. 38·5°, yield 75 per cent. of that theoretically possible). The condensation of the ketone with ethyl formate was carried out with satisfactory results under the following conditions. Sodium (1·6 grams) was granulated under toluene, which was then poured away and the metal washed with ether, and a mixture of anhydrous ether (50 c.c.) and absolute ethyl alcohol (3·2 grams) added. When the formation of sodium ethoxide appeared to be completed, a solution of *p*-acetylanisole (10 grams) in ethyl formate (7·4 grams) was introduced in small portions at a time with agitation and cooling of the containing vessel in melting ice. The mixture was allowed to remain overnight in the ice-chest and then decomposed by the addition of ice, more ether, and just sufficient acetic acid to give an acid reaction. The ethereal solution was separated and shaken with an excess of a saturated solution of copper acetate. A pale green copper derivative was precipitated, and this was collected, washed with water and ether, and dried at 100°. The yield of copper salt was 95 per cent. of that theoretically possible and calculated from the *p*-acetylanisole employed. The substance crystallises from toluene in flat, green prisms melting at 206—207° (Found: C = 57·4; H = 4·2; Cu = 15·0. $C_{20}H_{18}O_6Cu$ requires C = 57·6; H = 4·3; Cu = 15·1 per cent.). Ethereal solutions of the free *p*-anisyl β-hydroxyvinyl ketone were prepared from this copper derivative by shaking with ether, dilute sulphuric acid, and ice, and after separation and thorough drying with anhydrous sodium sulphate were employed at once. The free enol is very decomposable and undergoes auto-

condensation even when allowed to remain in ethereal solution. In presence of hydrogen chloride, it yielded a yellow oil, which was freed from some pyrylium derivative by precipitating the latter as cadmibromide. The filtered ethereal solution on evaporation deposited yellow, radiating needles, but these have not been further investigated.

7-Hydroxy-4'-methoxy-2-phenylbenzopyrylium Chloride (Formula III).—(A) Condensation of *p*-anisyl β-hydroxyvinyl ketone and resorcinol by means of hydrogen chloride in acetic acid solution proceeded abnormally with formation of amorphous, red compounds, but better results were obtained when anhydrous ether was used as the solvent. A slow stream of hydrogen chloride was passed during six hours into an ethereal solution of equimolecular proportions of the hydroxy-ketone and resorcinol, when a bright red, microcrystalline crust separated. This was collected, washed with ether, and dried in a vacuum over potassium hydroxide (Found : Cl = 12·1. $C_{16}H_{13}O_3Cl$ requires Cl = 12·3 per cent.). This product appears to be the anhydrous chloride. The substance may be crystallised from dilute hydrochloric acid in brownish-orange aggregates of microscopic needles which decompose at 182—183° (Found : Cl = 10·9, 11·1. $C_{16}H_{13}O_3Cl,2H_2O$ requires Cl = 10·9 per cent.). The yellow solution in sulphuric or acetic acid exhibits brilliant green fluorescence. The aqueous solutions are weakly fluorescent. The colour-base is thrown down as a reddish-purple precipitate on the addition of sodium acetate to a solution in dilute hydrochloric acid. It is very sparingly soluble in benzene and could not be crystallised. No tendency towards the formation of a colourless pseudo-base could be detected. The ferrichloride was amorphous, and the most characteristic derivative which has been examined is the *picrate*, obtained as a yellow precipitate by the addition of aqueous picric acid to a solution of the oxonium chloride. The substance crystallises from alcohol in golden, yellowish-brown needles melting and decomposing at 219—221° and also from acetic acid in light brown needles showing the same behaviour on heating. The solutions exhibit a characteristic intense green fluorescence.

(B) A slow stream of hydrogen chloride was passed through a solution of equimolecular proportions of β-resorcylaldehyde and *p*-acetylanisole in the minimum of glacial acetic acid during two hours at 0°, two hours at 20°, and three hours at 40°. A certain amount of the product crystallised out, and the remainder was precipitated by addition of ether, collected, washed with ether, dried, and crystallised from dilute hydrochloric acid. The salt was dried in the air and for a short time in a vacuum (Found :

C = 59·2; H = 5·2; Cl = 11·0. $C_{16}H_{13}O_3Cl,2H_2O$ requires C = 59·3; H = 5·3; Cl = 10·9 per cent.).

The reactions of the substance were identical with those of the chloride prepared by the method described under (A), and the picrate crystallised from ethyl alcohol in needles melting at 219—221° with decomposition, alone or mixed with a specimen obtained by the alternative process (Found: C = 54·7; H = 3·3. $C_{22}H_{15}O_{10}N_3$ requires C = 54·9; H = 3·1 per cent.).

Acacetidin Chloride (Formula IV).—A red product containing only traces of the desired substance was obtained by the condensation of *p*-anisyl β-hydroxyvinyl ketone and phloroglucinol by means of hydrogen chloride in acetic acid solution. The crude substance contained about 25 per cent. of the theoretical amount of chlorine, a derived chloroplatinate about 50 per cent. of the theoretical amount of platinum, and a ferrichloride, which was obtained from an acetic acid solution of the substance, gave Fe = 12·0, which is about 2 per cent. lower than the expected value. All attempts to purify these compounds were unsuccessful, and ultimately the following process was adopted. *p*-Anisyl β-hydroxyvinyl ketone (10 grams; 0·6 mol.), obtained as already described from the copper derivative, and anhydrous phloroglucinol (4·5 grams; 1 mol.), dissolved in not much more dry ether than is required, were condensed together by the agency of a stream of hydrogen chloride during thirteen hours. The containing vessel was immersed in melting ice during the first fifteen minutes. The deep red precipitate which separated was collected, washed with ether, and dried (7·5 grams). The crude product (about 20 grams) was extracted by boiling water (2500 c.c.) and hydrochloric acid (100 c.c.) and the filtered solution heated to redissolve the orange, amorphous precipitate which separated; on slow cooling, the substance crystallised in brownish-red, dumb-bell-shaped, dense clusters of microscopic needles. It was recrystallised from boiling ethyl alcohol (1100 c.c.) containing concentrated hydrochloric acid (40 c.c.) and was thus obtained in brown, diamond-shaped prisms having a striking green glance. Under the microscope, individual crystals are seen to have a clear orange colour and the smear on paper is bright red. The substance was dried in the air and for a short period in a vacuum (Found: C = 63·2; H = 4·4. $C_{16}H_{13}O_4Cl$ requires C = 63·2; H = 4·3 per cent.).

On heating, the substance preserves its lustre at 250° and does not melt at 360°. The salt is extremely sparingly soluble in cold dilute hydrochloric acid or in ethyl alcohol. It dissolves to some extent in boiling glacial acetic acid and separates, on cooling the orange solution, in glistening prisms. Its solution in sulphuric

acid is bright yellow and when very dilute exhibits vivid green fluorescence. It is not affected by cold water, but on warming, if the solvent is not in great excess, it partly dissolves and separates out again in brownish-red, flocculent, slender needles. These probably consist of a basic chloride and addition of a drop of hydrochloric acid reconverts the substance into the normal salt crystallising in prisms. When the substance is boiled with a large relative volume of water, the colour base is produced. This, best obtained by the action of sodium acetate, is a purplish-black precipitate insoluble in benzene, but soluble in ethyl acetate to a reddish-brown solution and in aqueous sodium carbonate to an intense bordeaux-red solution. A solution in hot dilute hydrochloric acid is orange, and on great dilution with water becomes dull red owing to the formation of the colour-base. The conditions necessary for the formation of a colourless pseudo-base could not be determined, and it is doubtful whether such a substance can be produced. The *sulphate* crystallises in orange-red, microscopic needles and is very sparingly soluble in dilute sulphuric acid. The deep red *iodide* crystallises in clusters of short, microscopic needles on the addition of potassium iodide to a hot dilute solution of the chloride. The *perchlorate* crystallises from hot dilute perchloric acid in orange-red, very regularly formed, stellate clusters of slender, pointed, microscopic needles. The *mercurichloride* is extremely sparingly soluble, and crystallises in light orange, microscopic needles when mercuric chloride is added to a hot solution of the chloride in dilute hydrchloric acid. Attempts to oxidise this salt to acacetin were not successful. Anisic acid was isolated as the result of the action of hydrogen peroxide in alkaline solution.

Trimethylapigenidin Ferrichloride (Formula V).—A mixture of 2-hydroxy-4 : 6-dimethoxybenzaldehyde (4 grams) and *p*-methoxyacetophenone (4 grams), potassium hydroxide (8 grams), and methyl alcohol (25 c.c.) was maintained at about 60° during twelve hours. The dark orange-red solution was then mixed with water and benzene, when an orange-yellow potassium salt of the chalkone separated in glistening leaflets. This substance was collected and added to concentrated hydrochloric acid (25 c.c.). The compound was coloured carmine, but, on boiling, the orange colour of the solution of trimethylapigenidin chloride was produced. On the addition of boiling water (50 c.c.), a clear orange-red solution resulted, and from this the chloride separated very readily, on cooling, in slender, orange needles. The *ferrichloride*, prepared in the usual manner, is a deep red precipitate and the substance crystallises from much boiling acetic acid in reddish-brown, fern-like aggregates of prisms which have a green reflex (Found : C = 43·6; H = 3·4.

$C_{18}H_{17}O_4Cl_4Fe$ requires C = 43·7; H = 3·4 per cent.). The substance sinters at 180° and melts at 187°. It is readily soluble in water to an intense orange-yellow solution, and its yellow dilute solution in sulphuric acid is at first non-fluorescent, but acquires a green fluorescence in a few minutes.

2-*Hydroxy*-4 : 6-*dimethoxystyryl* 3 : 4-*Dimethoxyphenyl Ketone* (Formula VI).—2-Hydroxy-4 : 6-dimethoxybenzaldehyde (4 grams) and acetoveratrone (4 grams) were dissolved in methyl alcohol (20 c.c.), and a hot solution of potassium hydroxide (5 grams) in water (10 c.c.) was added in one portion. The mixture was allowed to remain in a warm cupboard over-night, then cooled, and just acidified with acetic acid. The product partly crystallised from the solution and was collected, washed with methyl alcohol, and dried at 100° (2·1 grams). An excess of ether was added to the filtrate and the separated solution washed with water and then with concentrated aqueous potassium hydroxide; glistening, orange leaflets of the potassium derivative separated and a further quantity (1·0 gram) of the unsaturated ketone was obtained on careful acidification of the aqueous solution of the salt. The substance is very sparingly soluble in alcohol, ether, or ethyl acetate, more readily soluble in hot acetone. It is to some extent soluble in hot water to a yellow solution, and may be crystallised from toluene, in which it is sparingly soluble, in bright yellow, microscopic, rhombic prisms (Found : C = 66·1; H = 6·1. $C_{19}H_{20}O_6$ requires C = 66·3; H = 5·8 per cent.). The substance melts at 178—179° with decomposition to a red oil, and it is characterised by the extraordinary facility with which it may be converted into a pyrylium salt by the action of even weak acids.

Tetramethyl-luteolidin Ferrichloride (Formula VII).—The foregoing unsaturated ketone gives an orange-red solution in sulphuric acid, and on dilution with water there is no change in colour or precipitate, whilst on standing tetramethyl-luteolidin sulphate separates in orange-red, microscopic needles. The chalkone also dissolves in hot aqueous oxalic acid to a deep orange-red solution and the pyrylium oxalate separates on cooling in brilliant red clusters of microscopic needles. Even boiling glacial acetic acid closes the ring and it is indicated by a colour change when the reagent is a hot aqueous solution of benzoic acid. The bromide is readily obtained in beautiful, red prisms with green reflex by heating the chalkone with strong aqueous hydrobromic acid and adding alcohol. When the chalkone is covered with concentrated hydrochloric acid, it gives at first an intense red coloration and precipitate due to the formation of the ketone hydrochloride. On boiling, a clear red solution results and tetramethyl-luteolidin

chloride soon separates from the hot liquid in glistening, red, prismatic needles. On the addition of water the substance at first dissolves to a clear solution and separates again in a hydrated form, orange-red clusters of microscopic needles. We propose to return to the description of some of these salts as well as of luteolidin salts, which we have found can be obtained by the action of hydriodic acid in the usual manner. The *ferrichloride* was precipitated from a hot aqueous solution of the chloride. It crystallises from glacial acetic acid, in which it is very sparingly soluble, in salmon-red, fan-shaped clusters of microscopic needles melting at 206—207° (Found : C = 43·6; H = 3·7. $C_{19}H_{19}O_5Cl_4Fe$ requires C = 43·6; H = 3·6 per cent.). This compound has also been obtained in small yield in experiments on the condensation of 2-hydroxy-4 : 6-dimethoxybenzaldehyde and acetoveratrone by means of hydrogen chloride in both acetic acid and ethereal solution. The product obtained in this way was chocolate-brown and crystallised in balls of needles melting at 204—205°, but the melting point was not depressed by admixture with the pure substance. The smears on paper of both specimens were bright red and exhibited identical bronze reflex.

One of us (D. D. P.) desires to express his thanks to the Carnegie Trust for a scholarship which has enabled him to take part in this investigation, and grateful acknowledgment is also made to the Salter's Research Institute for a grant which facilitated the work of another of the joint authors (P. N. W.).

UNIVERSITIES OF LIVERPOOL, ST. ANDREWS, AND MANCHESTER. [*Received, November 26th,* 1923.]

XXVII.—*Some Derivatives of Benzopyrylium.*

By ROBERT ROBINSON and (in part) HERBERT GRACE CRABTREE, CHINYANN KUMARA DAS, WILFRID LAWSON, ROBERT WINSTANLEY LUNT, BERNARD HOLTOM ROBERTS, and PERCY NOEL WILLIAMS.

THE oxonium salts described below have been prepared at various times since 1912 by applications of the method of synthesis of benzopyrylium compounds which depends on the condensation under the influence of hydrogen chloride of a derivative of salicylaldehyde and a substance containing the group –CO–CH_2– (Perkin and Robinson, P., 1907, **23**, 149; Perkin, Robinson, and Turner, T., 1908, **93**, 1085; Decker and von Fellenberg, *Ber.*, 1907, **40**, 3815). *o*-Vanillin (2-hydroxy-3-methoxybenzaldehyde) has been

found to condense very readily with a series of ketones in presence of hydrogen chloride, and the 8-methoxybenzopyrylium derivatives so obtained exhibited considerable divergence in properties from the similarly constituted 7-methoxy-compounds. For example, the latter salts are strikingly fluorescent in dilute acid solution, but the former class give non-fluorescent solutions.

[With ROBERT WINSTANLEY LUNT.]

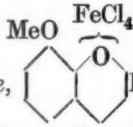
2-Hydroxy-5-methylstyryl 4-Methoxyphenyl Ketone, $OH{\cdot}C_6H_3Me{\cdot}CH{:}CH{\cdot}CO{\cdot}C_6H_4{\cdot}OMe$.—Potassium hydroxide (8 grams), dissolved in the minimum amount of water, was added to a solution of 2-hydroxy-5-methylbenzaldehyde (5 grams) and *p*-methoxyacetophenone (8 grams) in ethyl alcohol (10 c.c.) and ether (15 c.c.). The mixture was shaken frequently and allowed to remain during twenty-one hours, when the potassium salt of the unsaturated ketone separated in crimson, feathery needles. After the addition of ether (70 c.c.) the salt was collected, washed with ether, and decomposed by means of very dilute acetic acid. The pale yellow oil crystallised on rubbing and was collected, washed, and dried (5·5 grams). A further amount (0·5 gram) was recovered from the ethereal filtrate and the total yield was thus 65 per cent. of that theoretically possible. The substance crystallises from benzene in microscopic, pale yellow, hexagonal plates which darken slightly at 142° and melt at 151—152° to a green liquid (Found : C = 75·9; H = 6·3. $C_{17}H_{16}O_3$ requires C = 76·1; H = 6·0 per cent.). This derivative of salicylideneacetophenone is readily converted into the corresponding pyrylium chloride by passing hydrogen chloride into its ethereal solution or by simply dissolving it in acetic acid and after the addition of dilute hydrochloric acid boiling the solution during two minutes. On the addition of a concentrated solution of ferric chloride in hydrochloric acid, a carmine precipitate is thrown down, and this, after collection, may be crystallised from acetic acid (Found : Fe = 12·7. $C_{17}H_{15}O_2Cl_4Fe$ requires Fe = 12·5 per cent.). *4′-Methoxy-2-phenyl-6-methylbenzopyrylium ferrichloride* is sparingly soluble in cold acetic acid and crystallises in beautiful, crimson needles melting at 165—166°.

[With BERNARD HOLTOM ROBERTS.]

2-Hydroxy-3-methoxystyryl Phenyl Ketone, $MeO{\cdot}C_6H_3(OH){\cdot}CH{:}CH{\cdot}COPh$.

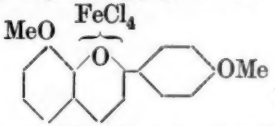
An almost quantitative yield of this substance was obtained under the following conditions. Potassium hydroxide (15 grams), dissolved in just sufficient water, was added to a solution of

o-vanillin (10 grams) and acetophenone (8 grams) in ethyl alcohol (50 c.c.). The mixture became orange and then red, and a red potassium salt separated. After remaining over-night, this was collected, dried (21 grams), and decomposed by means of dilute acetic acid. The unsaturated ketone crystallises from alcohol in yellow prisms melting at 112° (Found : C = 75·4; H = 5·5. $C_{16}H_{14}O_3$ requires C = 75·6; H = 5·5 per cent.).

8-*Methoxy-2-phenylbenzopyrylium ferrichloride*, 

was obtained by the addition of a concentrated solution of ferric chloride in hydrochloric acid to a solution of the corresponding oxonium chloride. The reddish-brown precipitate was collected and the substance crystallised from acetic acid. It separated in reddish-brown needles melting at 157° (Found : C = 44·0; H = 3·1; Cl = 32·6. $C_{16}H_{13}O_2Cl_4Fe$ requires C = 44·1; H = 3·0; Cl = 32·7 per cent.). The required chloride was obtained in poor yield by the action of hot concentrated hydrochloric acid on the unsaturated ketone just described, and in excellent yield by passing hydrogen chloride through a solution of *o*-vanillin (10 grams) and acetophenone (8 grams) in acetic acid (25 c.c.) cooled in ice. After two hours the mixture was allowed to remain over-night and the orange, crystalline salt collected and washed with ether. The substance is readily soluble in hot dilute hydrochloric acid to a clear orange solution.

[With Percy Noel Williams.]

8 : 4′-*Dimethoxy-2-phenylbenzopyrylium Ferrichloride*, 

—A stream of hydrogen chloride was passed through a solution of *o*-vanillin (5 grams) and *p*-methoxyacetophenone (6 grams) in acetic acid (10 c.c.) during two hours at 0°, two hours at room temperature, and three hours at 40°. The product was dissolved as far as possible in hot water and the filtered solution treated with an excess of ferric chloride dissolved in concentrated hydrochloric acid. The precipitated ferrichloride was collected, dried (7·5 grams), and crystallised from acetic acid. The salt is readily soluble in the hot solvent, sparingly soluble in the cold, and separates in brown, jagged needles, m. p. 180° (Found : Cl = 30·8; Fe =

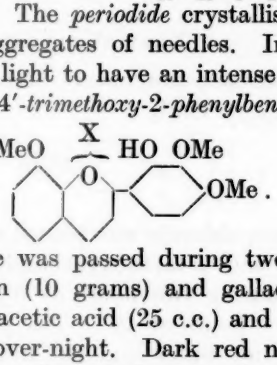
11·9. $C_{17}H_{15}O_3Cl_4Fe$ requires Cl = 30·5; Fe = 12·0 per cent.). When treated with aqueous sodium acetate, it yields the corresponding pseudo-base, which is soluble in ether. Addition of perchloric acid to the separated ethereal solution precipitates a crystalline, yellow *perchlorate*, which may be recrystallised from hot dilute aqueous perchloric acid in yellow needles, m. p. 227°.

[With Herbert Grace Crabtree.]

2-*Hydroxy*-3-*methoxystyryl* 2 : 3 : 4-*Trimethoxyphenyl Ketone*.—Potassium hydroxide (15 grams), dissolved in water (50 c.c.), was added to a solution of *o*-vanillin (10 grams) and gallacetophenone trimethyl ether (10 grams) in alcohol (60 c.c.). The mixture was allowed to remain over-night and the dark red solution then acidified with acetic acid. The yellow precipitate was collected and crystallised, first from ethyl alcohol and then from benzene. The moderately sparingly soluble chalkone derivative separated in bright yellow, microscopic needles, m. p. 145° (Found : C = 66·2; H = 5·9. $C_{19}H_{20}O_6$ requires C = 66·3; H = 5·8 per cent.).

8 : 2′ : 3′ : 4′-*Tetramethoxy*-2-*phenylbenzopyrylium Salts*.—A solution of the chloride was prepared by dissolving *o*-vanillylidenegallacetophenone trimethyl ether (2 grams) in acetic acid (20 c.c.) and, after the addition of concentrated hydrochloric acid (50 c.c.), boiling for one minute. The *ferrichloride*, obtained in the usual manner as a brick-red precipitate, crystallised from acetic acid in glistening, red plates exhibiting a green reflex and melting at 172° (Found : C = 43·1; H = 3·6. $C_{19}H_{19}O_5Cl_4Fe$ requires C = 43·4; H = 3·6 per cent.). The *periodide* crystallises from ethyl alcohol in black, stellate aggregates of needles. Individual crystals are seen by transmitted light to have an intense purple colour.

2′-*Hydroxy*-8 : 3′ : 4′-*trimethoxy*-2-*phenylbenzopyrylium Salts*,

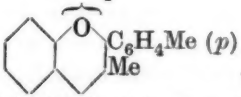


—Hydrogen chloride was passed during two hours into a cooled solution of *o*-vanillin (10 grams) and gallacetophenone dimethyl ether (13 grams) in acetic acid (25 c.c.) and the mixture was then allowed to remain over-night. Dark red needles separated, and these were collected and washed with ether. A further quantity could be recovered from the mother-liquor by precipitation with ether. This chloride is moderately soluble in cold water without suffering hydrolysis. It is readily soluble in hot dilute hydrochloric acid and crystallises when the solution is cooled. The *ferrichloride*

crystallises from acetic acid in dark red, glistening needles, m. p. 194° (Found : C = 42·0; H = 3·3. $C_{18}H_{17}O_5Cl_4Fe$ requires C = 42·2; H = 3·3 per cent.). The *picrate* is a vermilion precipitate which crystallises from alcohol in glistening, elongated, flat prisms, m. p. 164°. The *periodide* crystallises from alcohol in long, purple needles, m. p. 133°. The *cadmibromide* is an orange precipitate which is very sparingly soluble, but may be crystallised from much formic acid in silky, orange threads decomposing at 230°. The *mercurichloride* crystallises from acetic acid in short, silky, orange-yellow needles, m. p. 143°.

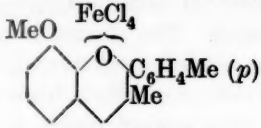
[With Chinyann Kumara Das.]

2-Phenyl-3 : 4′-dimethylbenzopyrylium Ferrichloride,



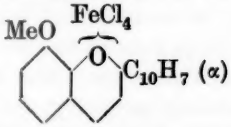
—A mixture of salicylaldehyde (13 grams), *p*-tolyl ethyl ketone (16 grams), potassium hydroxide (15 grams dissolved in a little water), and ethyl alcohol (50 c.c.) was allowed to remain during thirty hours and then, since condensation did not appear to be complete, heated on the steam-bath under reflux during two and a half hours. The product isolated by acidification and extraction with ether could not be induced to crystallise. The ethereal solution (about 150 c.c.) was thoroughly washed with water and mixed with ferric chloride (25 grams of hydrated salt), dissolved in concentrated hydrochloric acid (100 c.c.). The ether was removed by distillation and the residual liquid boiled during ten minutes. On cooling and adding water and ether, a voluminous, crystalline precipitate was obtained, and this was collected, dried, and crystallised from acetic acid. The bright yellow needles melt at 165—166° (Found : Cl = 32·7; Fe = 12·8. $C_{17}H_{15}OCl_4Fe$ requires Cl = 32·8; Fe = 12·9 per cent.). This salt is at once hydrolysed by water, yielding a colourless pyranol, and a trace dissolved in sulphuric acid gives a pale yellow solution exhibiting bluish-violet fluorescence. Under the same conditions, the 8-methoxy-derivative described below gives only a very weak green fluorescence and this is a general property of pyrylium salts derived from *o*-vanillin. It is all the more remarkable in view of the intensity of the fluorescence developed even in dilute aqueous solution by the 7-methoxybenzopyrylium salts. The 8-methoxy-group definitely inhibits the fluorescent property, as may be seen by comparison of *iso*brazilein and *iso*hæmatein salts.

8-*Methoxy*-2-*phenyl*-3 : 4′-*dimethylbenzopyrylium Ferrichloride*,



—Hydrogen chloride was passed into a solution of *o*-vanillin (14·6 grams) and *p*-tolyl ethyl ketone (14 grams) in acetic acid (60 c.c.) during four hours at room temperature and then during four hours at 60°. The dark red solution was diluted with water and neutral impurities were removed by extraction with a little ether. A ferrichloride was then precipitated in the usual manner and collected and dried (31·5 grams). The substance crystallises readily from acetic acid in glistening, orange-brown needles, m. p. 172° (Found : Cl = 30·9; Fe = 11·4. $C_{18}H_{17}O_2Cl_4Fe$ requires Cl = 30·6; Fe = 11·3 per cent.). The salt is at once hydrolysed by water with formation of a colourless pyranol and in this respect differs from benzopyrylium salts containing two methoxy-groups. A very curious property of the pyranol which has not been observed hitherto in any similar case is its ready conversion into a crystalline sodium derivative. The ferrichloride was finely powdered and shaken with water and ether, and the ethereal extract washed with more water and agitated with 10 per cent. aqueous sodium hydroxide. The derivative, which separated in almost colourless needles, was collected and dried. The yield was 11·5 grams from 15·5 grams of the ferrichloride. The substance is readily soluble in ethyl alcohol, more sparingly soluble in cold methyl alcohol, and separates in needles on the addition of ether. It is hydrolysed by water with formation of a very pale yellow, uncrystallisable, viscous substance. The analytical results were unsatisfactory, agreeing, however, with the monosodium derivative of the pyranol (or isomeric unsaturated ketone) with varying amounts of water as addendum. The natural hypothesis that this substance is merely the sodium derivative of the open-chain unsaturated ketone is scarcely in agreement with its very pale yellow colour, the ease of formation from the pyranol, and with the fact that the compound is at once converted by hydrochloric acid into the benzopyrylium salt.

8-*Methoxy*-2-α-*naphthylbenzopyrylium Ferrichloride*,

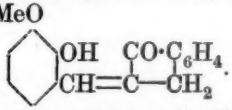


—A stream of hydrogen chloride was passed during three hours

through a solution of *o*-vanillin (3·5 grams) and α-naphthyl methyl ketone (4 grams) in glacial acetic acid (15 c.c.), the dark red solution was diluted with water, and any unchanged material removed by extraction with ether. The ferrichloride was then derived in the usual way and the dark red precipitate collected, dried, and crystallised from acetic acid, in which it is very sparingly soluble. The substance crystallises in brownish-red, dense clusters of microscopic needles, m. p. 230° (Found : C = 49·4; H = 3·0. $C_{20}H_{15}O_2Cl_4Fe$ requires C = 49·5; H = 3·1 per cent.). The salt gives a yellow, non-fluorescent solution in sulphuric acid and dissolves in water to a yellow solution which at once clouds owing to the formation of the pseudo-base.

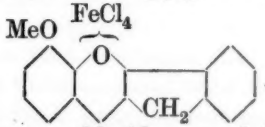
[With WILFRID LAWSON.]

2'-Hydroxy-3'-methoxy-2-benzylidene-1-hydrindone,



—Potassium hydroxide (10 grams), dissolved in water (20 c.c.), was added to a solution of *o*-vanillin (9·5 grams) and α-hydrindone (6·6 grams) in ethyl alcohol (100 c.c.) and the mixture boiled during half an hour and then allowed to remain over-night. On the addition of water and acetic acid, the condensation product was precipitated, and after collection and drying at 100° weighed 13 grams. The substance crystallised from ethyl acetate in bright yellow, felted needles, m. p. 198° (Found : C = 76·5; H = 5·3. $C_{17}H_{14}O_3$ requires C = 76·7; H = 5·2 per cent.). The potassium salt crystallises from boiling ethyl alcohol in orange-red needles exhibiting a striking beetle-green iridescence (Found : K = 12·7. $C_{17}H_{13}O_3K$ requires K = 12·8 per cent.).

8-Methoxy-2 : 3-indeno(1 : 2)benzopyrylium Ferrichloride,



—A stream of hydrogen chloride was led into a solution of *o*-vanillin (15 grams) and α-hydrindone (12 grams) in acetic acid (30 c.c.) during two hours. Crystals separated and after further precipitation by means of ether (15 c.c.) the oxonium chloride was collected, washed with ether, and dried (25 grams). The related *ferrichloride*, prepared in the usual manner, crystallised from acetic acid, in which it is somewhat sparingly soluble, in small, slender, red needles, m. p. 187—188° (Found : C = 45·7; H = 2·9;

Fe = 12·3. $C_{17}H_{13}O_2Cl_4Fe$ requires C = 45·8; H = 2·9; Fe = 12·5 per cent.). The salt is readily hydrolysed and its yellow solution in sulphuric acid exhibits a very faint green fluorescence. The same ferrichloride was obtained by boiling the *o*-vanillylidenehydrindone with a mixture of ethyl alcohol and half its volume of concentrated hydrochloric acid until a sample gave no precipitate on moderate dilution with water. The precipitate obtained on the addition of concentrated ferric chloride solution was crystallised from acetic acid and melted at 187°.

UNIVERSITIES OF SYDNEY AND LIVERPOOL.

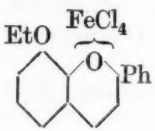
[*Received, November 26th*, 1923.]

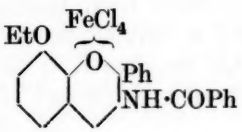
XXVIII.—*Some Benzopyrylium Salts.*

By LESLIE RANDAL RIDGWAY and ROBERT ROBINSON.

IN the course of an investigation in the pyrylium group we have made some isolated observations which are brought together in the present communication.

An attempt to prepare a benzopyrylium salt in which a halogen atom occurs as a substituent in position 3 gave a curious result. The condensation of 2-hydroxy-3-ethoxybenzaldehyde with ω-bromoacetophenone in acetic acid solution by means of hydrogen chloride yielded 8-ethoxy-2-phenylbenzopyrylium chloride, isolated as the ferrichloride (I), since the same salt could be prepared from ethoxysalicylaldehyde and acetophenone.

(I.) 



(II.)

No doubt at some stage the bromine is enabled to effect substitution for hydrogen in the phenolic component of the mixture, but it is not clear that the bromoacetophenone itself functions in this way. Thus the bromo-ketone is found to be only partly reduced by guaiacol in glacial acetic acid solution saturated with hydrogen chloride under the conditions of the above experiment.

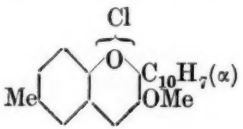
Possibly reduction is effected at the aldol stage,

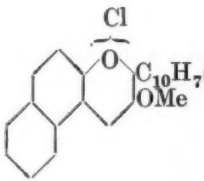
R·CH(OH)·CHBr·COPh,

because two oxygen atoms then conspire to develop the "hypobromite" character of the bromine atom. Our efforts to attach a nitrogen atom to the pyrylium nucleus were more successful, and

3-benzoylamino-8-ethoxy-2-phenylbenzopyrylium ferrichloride (II) has been prepared from 2-hydroxy-3-ethoxybenzaldehyde and ω-benzoylaminoacetophenone by an application of the general method. It was of great interest to attempt the removal of the benzoyl group from this salt and so obtain an aminopyrylium compound, but neither the chloride corresponding to this substance nor its 4′-methoxy-derivative, which has also been synthesised, could be hydrolysed without decomposition. We are continuing our experiments in this direction, and preliminary trials with a similar salt in which the nitrogen is protected by the carbethoxy-group have given encouraging results.

In connexion with the investigation of the chemistry of morphine and its allies, which is being prosecuted in these laboratories, it is a matter of importance to discover new reagents for the group $-CO\cdot CH_2\cdot CO-$. The facile direct condensation of 2-hydroxy-3-ethoxybenzaldehyde with *cyclo*hexanone leading to highly characteristic products is therefore of some interest (see p. 218). An account is included of some compounds which have been prepared in order to throw light on the elusive property of fluorescence in relation to structure in this group. In an earlier investigation of the oxazoles, it had been found that the replacement of a phenyl group by an α-naphthyl group resulted in a greatly enhanced fluorescence (Lister and Robinson, T., 1912, **101**, 1298). We were surprised to find that the salts III and IV, containing one and two naphthalene nuclei respectively, are almost non-fluorescent.

(III.) 

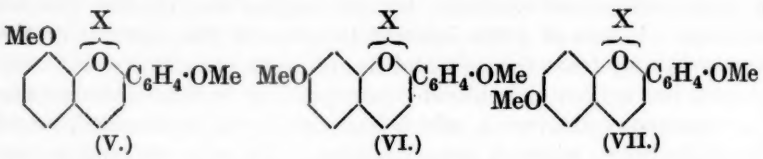


(IV.)

Most simply constituted benzopyrylium salts exhibit fluorescence in concentrated sulphuric acid solution, but the 7-methoxy-derivatives are unique in that they usually show striking fluorescence in dilute aqueous solution. Thus 8 : 4′-dimethoxy-2-phenylbenzopyrylium salts (V) are non-fluorescent in aqueous solution and only feebly fluorescent in concentrated sulphuric acid, whilst 7 : 4′-dimethoxy-2-phenylbenzopyrylium salts (VI) are brilliantly fluorescent under both conditions. 6 : 4′-Dimethoxy-2-phenylbenzopyrylium chloride (VII) has now been prepared and is found to exhibit striking fluorescence in sulphuric acid and alcoholic solutions, whilst aqueous solutions are weakly fluorescent.

Thus the effect of the methoxyl in position 6 is in reality nearer

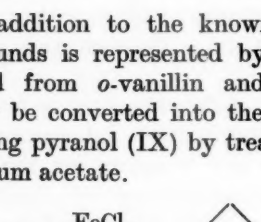
to that of the same group in position 7 than in position 8, which was scarcely to be expected.

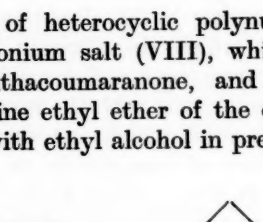


(V.) (VI.) (VII.)

An addition to the known types of heterocyclic polynuclear compounds is represented by the oxonium salt (VIII), which is derived from *o*-vanillin and β-naphthacoumaranone, and may readily be converted into the crystalline ethyl ether of the corresponding pyranol (IX) by treatment with ethyl alcohol in presence of sodium acetate.

(VIII.)





(IX.)

EXPERIMENTAL.

8-*Ethoxy*-2-*phenylbenzopyrylium Ferrichloride* (Formula I).—(A) A stream of hydrogen chloride was passed into a solution of acetophenone (1·7 grams) and 2-hydroxy-3-ethoxybenzaldehyde (2·2 grams) in acetic acid (5 c.c.) during two hours. A ferrichloride was precipitated on the addition of an excess of ferric chloride dissolved in concentrated hydrochloric acid, and this derivative was collected, washed with ether, and crystallised from glacial acetic acid. The substance crystallises in deep brown, glistening plates, melting at 139—140° and at the same temperature when mixed with a specimen obtained by the following method.

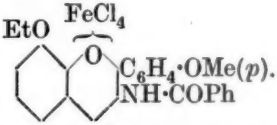
(B) Hydrogen chloride was led into a mixture of ω-bromoacetophenone (12·2 grams), 2-hydroxy-3-ethoxybenzaldehyde (6·8 grams), and acetic acid (16 c.c.) during six hours. As in the previous case, there was no separation of an oxonium chloride from the dark brown solution, and the ferrichloride was directly precipitated, washed with ether, and crystallised from acetic acid. The yield was 4·7 grams and the substance melted at 140° (Found : C = 45·2, 45·4; H = 3·4, 3·4. $C_{17}H_{15}O_2Cl_4Fe$ requires C = 45·4; H = 3·3 per cent.).

3-*Benzoylamino*-8-*ethoxy*-2-*phenylbenzopyrylium Ferrichloride* (Formula II).—When a current of dry hydrogen chloride was passed

into a solution of ω-benzoylaminoacetophenone (Robinson, T., 1909, **95**, 2169) (1·5 grams) and 2-hydroxy-3-ethoxybenzaldehyde (1·1 grams) in acetic acid (10 c.c.) during three hours, no crystals were deposited, but the liquid acquired a deep ruby-red colour. On the addition of a concentrated solution of hydroferrichloric acid, a dark oil was precipitated, and this quickly solidified to a red, crystalline mass. The substance was collected, dried (1·1 grams), and crystallised from acetic acid (Found: C = 50·5; H = 3·6. $C_{24}H_{20}O_3NCl_4Fe$ requires C = 50·7; H = 3·5 per cent.).

The salt is readily soluble in hot acetic acid and crystallises in small, orange-red needles, m. p. 198°. It is converted by water into a colourless pseudo-base, and attempts to remove the benzoyl group by hydrolysis with hydrochloric acid were unsuccessful. The sole product was a dark brown, meutral substance which has not yet been investigated. There were no indications of the formation of an aminopyrylium salt.

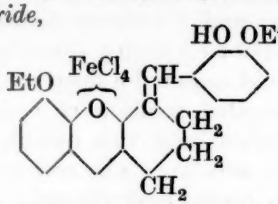
3-Benzoylamino-4'-methoxy-8-ethoxy-2-phenylbenzopyrylium Ferrichloride,



—ω-Benzoylamino-*p*-methoxyacetophenone is more conveniently prepared by the following method than by that described by Lister and Robinson (*loc. cit.*, p. 1304). ω-Amino-*p*-methoxyacetophenone stannichloride (8 grams) was mixed with powdered fused sodium acetate (10 grams), acetic acid (10 c.c.), and benzoyl chloride (3·5 grams). After shaking during fifteen minutes, most of the product separated in a crystalline condition, and the reaction mixture was then allowed to remain over-night. Water was then added and the precipitate collected and extracted with boiling ethyl alcohol. The filtered solution deposited 3·3 grams, m. p. 113°, and a further 1·5 grams was obtained after concentration of the mother-liquor (Found: C = 71·7; H = 5·7. Calc. for $C_{16}H_{15}O_3N$, C = 71·4; H = 5·5 per cent.).

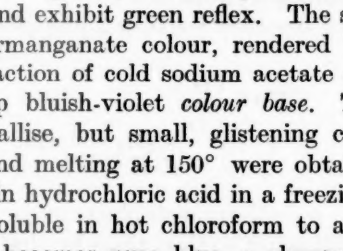
A mixture of ω-benzoylamino-*p*-methoxyacetophenone (2 grams), 2-hydroxy-3-ethoxybenzaldehyde (1·2 grams), and acetic acid (10 c.c.) was saturated with hydrogen chloride during six hours. The *ferrichloride* was derived in the usual manner and crystallised from acetic acid in glistening, reddish-brown plates (2·0 grams), m. p. 201° (Found: C = 50·0; H = 3·9. $C_{25}H_{22}O_4NCl_4Fe$ requires C = 50·2; H = 3·7 per cent.). The properties of this salt closely resemble those of the analogue described above.

5-Ethoxy-4-(2-hydroxy-3-ethoxybenzylidene)-1:2:3:4-tetrahydroxanthylium Ferrichloride,



—Hydrogen chloride was passed into a solution of 2-hydroxy-3-ethoxybenzaldehyde (10 grams) and *cyclo*hexanone (3 grams) in ether (100 c.c.) during three-quarters of an hour and the mixture then allowed to remain during an hour. The first few bubbles of the gas produced a purple solution, and crystallisation of the product in dark purple needles commenced after twenty minutes. This chloride was collected, washed with ether, and dried (9·5 grams). The crystals are dark brown by transmitted light and exhibit green reflex. The solution in alcohol has an intense permanganate colour, rendered bluer on dilution with water. The action of cold sodium acetate on the chloride is to produce a deep bluish-violet *colour base*. This salt is very difficult to recrystallise, but small, glistening crystals exhibiting a brilliant sheen and melting at 150° were obtained by cooling a saturated solution in hydrochloric acid in a freezing mixture. The crude chloride is soluble in hot chloroform to a damson solution which, on boiling, becomes pure blue, a change accompanied by evolution of hydrogen chloride. On cooling, a deep blue substance with highly characteristic coppery lustre separates in a crystalline condition, but this experiment only succeeds on a small scale, since the elimination of hydrogen chloride is progressive and ultimately the *spiro*pyran described below is obtained. The *ferrichloride* was obtained in a crystalline condition by mixing hot, filtered solutions of the chloride and of hydroferrichloric acid in acetic acid. It is a very sparingly soluble, chocolate powder, m. p. 197° (Found: C = 48·5; H = 4·6. $C_{24}H_{25}O_4Cl_4Fe,H_2O$ requires C = 48·6; H = 4·6 per cent.).

*Diethoxytrimethylenedibenzo*spiro*pyran,*



—(Compare Decker and Felser, *Ber.*, 1908, **41**, 2997, 3005; Borsche, *Ber.*, 1912, **45**, 50).

This substance was readily obtained by boiling the crude chloride described in the preceding section with a large volume of water containing a little hydrochloric acid. The precipitate was collected and crystallised from ethyl alcohol and after three crystallisations obtained in colourless, prismatic needles which often form clusters and melt at 155° (Found: C = 76·5; H = 6·7. $C_{24}H_{24}O_4$ requires C = 76·6; H = 6·4 per cent.).

The compound is moderately readily soluble in most organic solvents and is reconverted by mineral acids into an oxonium salt.

α-Naphthyl Methoxymethyl Ketone, $C_{10}H_7{\cdot}CO{\cdot}CH_2{\cdot}OMe$.—A dry ethereal solution of methoxyacetonitrile (10 grams) was gradually added to a well-cooled solution of magnesium α-naphthyl bromide from 30 grams of α-bromonaphthalene in ether (*ca.* 150 c.c.). The vigorous reaction was accompanied by a crackling sound and a colourless additive product was deposited. In the later stages, it was found necessary to break up the hard mass with a glass rod. After twelve hours, the product was decomposed with ice-water and ice-cold dilute sulphuric acid, and the ethereal layer separated, washed with sodium carbonate, and, after removal of the solvent, distilled in steam. The residue in the flask was taken up in ether, the extract separated, dried with sodium sulphate, and distilled. The main fraction was a pale yellow, viscid oil, b. p. 184—186°/13 mm. (Found: C = 78·3; H = 6·1. $C_{13}H_{12}O_2$ requires C = 78·0; H = 6·0 per cent.).

α-Naphthyl methoxymethyl ketone is readily soluble in most organic solvents and could not be crystallised. Its *semicarbazone* crystallises from aqueous ethyl alcohol in colourless needles, m. p. 164° (Found: N = 16·6. $C_{14}H_{15}O_2N_3$ requires N = 16·3 per cent.).

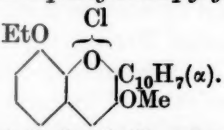
3-Methoxy-2-α-naphthyl-6-methylbenzopyrylium Chloride (Formula III).—A stream of hydrogen chloride was passed through a solution of α-naphthyl methoxymethyl ketone (4·0 grams) and 2-hydroxy-5-methylbenzaldehyde (2·7 grams) in acetic acid (10 c.c.) during four hours. The *ferrichloride* of the resulting oxonium base was obtained in the usual way as a granular, chocolate powder, markedly sparingly soluble in boiling glacial acetic acid. The derivative was found to be more soluble in absolute formic acid and was twice crystallised from this solvent. It was thus obtained in glistening plates (4·6 grams) melting at 184° and moderately soluble in alcohol, acetone, or chloroform (Found: C = 50·2; H = 3·5. $C_{21}H_{17}O_2Cl_4Fe$ requires C = 50·5; H = 3·4 per cent.).

The *chloride* is precipitated when concentrated hydrochloric acid is added to an alcoholic solution of the ferrichloride. The process was repeated, the product well washed with dilute hydrochloric acid, and crystallised twice from hot dilute hydrochloric acid.

The orange needles so obtained melted at 84° and decomposed at 110° (Found: C = 64·5; H = 5·8. $C_{21}H_{17}O_2Cl,3H_2O$ requires C = 64·5; H = 5·9 per cent.).

This salt is not very readily hydrolysed by water and its orange, non-fluorescent solution in sulphuric acid acquires a green fluorescence in about thirty minutes in the cold, no doubt as the result of sulphonation.

3-*Methoxy*-8-*ethoxy*-2-α-*naphthylbenzopyrylium Chloride*,



—This substance separated after half an hour as a brilliant red mass of crystals filling the liquid when hydrogen chloride was passed into a mixture of α-naphthyl methoxymethyl ketone (2·0 grams), 2-hydroxy-3-ethoxybenzaldehyde (1·6 grams), and acetic acid (5 c.c.). The substance was collected, washed with ether, and crystallised from hot, moderately concentrated hydrochloric acid. The bright reddish-orange plates (2·1 grams) were dried in a vacuum over sodium hydroxide and melted at 115—116° and decomposed at 120° (Found: C = 65·4; H = 5·8. $C_{22}H_{18}O_3Cl,2H_2O$ requires C = 65·6; H = 5·7 per cent.).

This salt is sparingly soluble in cold alcohol, and on heating with this solvent turns crimson and dissolves to a yellow solution, from which water precipitates the colourless pyranol or pyranol ether. The latter may be reconverted into the oxonium salt by the action of hydrochloric acid. It is soluble in acetone or chloroform to orange-yellow solutions and is at once hydrolysed by water. The crimson solution in sulphuric acid does not exhibit fluorescence. The *ferrichloride* crystallises from acetic acid, in which it is sparingly soluble, in reddish-brown needles, m. p. 197° (Found: C = 49·7; H = 3·7. $C_{22}H_{19}O_3Cl_4Fe$ requires C = 49·9; H = 3·6 per cent.).

3-*Methoxy*-2-α-*naphthylnaphtha*-(2 : 1)-*pyrylium Chloride* (Formula IV).—When a stream of hydrogen chloride was led into a solution of α-naphthyl methoxymethyl ketone (4·2 grams) and β-hydroxy-α-naphthaldehyde (3·6 grams) in acetic acid (10 c.c.), crystallisation of the product commenced in half an hour and was completed by passing the gas during a further hour. The substance was collected, washed with concentrated hydrochloric acid, and crystallised from dilute hydrochloric acid. The brilliant red, microscopic plates (6·5 grams) melted at 94° and decomposed at 119°. The analytical results obtained in the case of this salt indicated indefinite addenda, but the *ferrichloride* had the normal composition. The derivative separated from acetic acid in bright red, microscopic plates melting

at 183° with some previous darkening (Found: C = 54·0; H = 3·2. $C_{24}H_{17}O_2Cl_4Fe$ requires C = 53·8; H = 3·2 per cent.).

6 : 4′-*Dimethoxy*-2-*phenylbenzopyrylium Chloride* (Formula VII).—Hydrogen chloride was passed into a mixture of 2-hydroxy-5-methoxybenzaldehyde (1·8 grams), *p*-methoxyacetophenone (1·8 grams), and acetic acid (10 c.c.) during two hours, when a considerable crystallisation of the condensation product ensued. The substance was collected and crystallised from dilute hydrochloric acid in orange-red plates (2·8 grams), m. p. 135°. The green fluorescence in alcoholic and sulphuric acid solutions is striking, and even the yellow, aqueous solution exhibits perceptible fluorescence. The pseudo-base is not obtained by the action of water, but separates as a faintly pink opalescence or oil on the addition of sodium acetate. The *ferrichloride* crystallises from acetic acid in brownish-red plates, m. p. 192—193° (Found: C = 44·1; H = 3·5. $C_{17}H_{15}O_3Cl_4Fe$ requires C = 43·9; H = 3·2 per cent.).

This derivative is readily soluble in acetic acid and also in alcohol and chloroform to yellow and orange, weakly fluorescent solutions, respectively.

8-*Methoxy*-β-*naphthacoumarono*-(β : α-2 : 3)-*benzopyrylium Ferrichloride* (Formula VIII).—It had been found in previous trials that whereas homocyclic ketones, for example, the α-hydrindones, readily yield oxonium salts by condensation with derivatives of salicylaldehyde under the influence of acids, the coumaranones do not undergo a similar reaction with facility. We are indebted to Dr. H. Stephen for the gift of a specimen of β-naphthacoumaranone which has enabled us to find the requisite conditions. When hydrogen chloride is passed into an ethereal or, better, an alcoholic solution of equimolecular quantities of *o*-vanillin and β-naphthacoumaranone, the sole product is o-*vanillylidene*-β-*naphthacoumaranone*, which separates in a few seconds in quantitative yield. The bright yellow substance crystallises from ethyl acetate in orange-yellow, rectangular, prismatic needles which are very sparingly soluble in most organic solvents (Found: C = 75·3; H = 4·6. $C_{20}H_{14}O_4$ requires C = 75·4; H = 4·4 per cent.).

The substance darkens above 230° and is much discoloured above 240°. It melts to a deep green liquid at 247—248°. Solutions in hot aqueous or alcoholic potassium hydroxide are bluish-crimson and, on cooling, the potassium salt separates in crimson flocks, changing to black, microscopic needles. The blood-red solution in sulphuric acid becomes yellow on dilution with water. It was not found possible to convert this unsaturated ketone into a pyrylium salt by the action of acids.

The oxonium salt is produced when a rapid stream of hydrogen

chloride is passed through a solution of *o*-vanillin (0·6 gram) and β-naphthacoumaranone (0·7 gram) in acetic acid (40 c.c.) at 50°. In ten minutes, the chloride began to crystallise from the dark solution, and after twenty minutes the whole was added to 250 c.c. of hot dilute hydrochloric acid, the solution filtered, and the *ferrichloride* precipitated. This sparingly soluble substance was crystallised from a large volume of acetic acid and separated on rapid cooling in stellate aggregates of needles which changed into long prisms. On slow cooling, glistening, sage-green, flat needles were obtained. The smear on paper is chocolate and the crystals are deep red by transmitted light. The substance melts with decomposition at 236—240° (Found: C = 47·6; H = 2·6. $C_{20}H_{13}O_3Cl_4Fe$ requires C = 47·7; H = 2·6 per cent.).

On warming with ethyl alcohol and a trace of sodium acetate, this ferrichloride was decolorised and the addition of water precipitated a colourless substance This was collected and crystallised from alcohol in colourless, satiny needles, m. p. 165° (Found: C = 76·2; H = 5·3. $C_{22}H_{18}O_4$ requires C = 76·3; H = 5·2 per cent.). The substance is sparingly soluble in cold alcohol and is evidently the ethyl ether of the pyranol (formula IX). It is reconverted by acids into the orange solutions of the oxonium salts, and, in particular, the ferrichloride, m. p. 236—240°, was regenerated. Its orange solution in sulphuric acid does not exhibit fluorescence.

THE UNIVERSITY, MANCHESTER. [*Received, November 26th*, 1923.]

XXIX.—*A Quantitative Study of the Interaction of Glucose and Phenylhydrazine.*

By EDMUND KNECHT and FRANK PEBERDY THOMPSON.

IN the course of an investigation, we had occasion to prepare phenylglucosazone from the products of hydrolysis of cellulose. As no references could be found relating to the quantitative nature of this reaction, and as the yield of osazone prepared from pure glucose was found to be very low, an attempt was made to examine the reaction quantitatively.

E. Fischer (*Ber.*, 1884, **17**, 579) noted that the yield of osazone prepared from glucose amounted to 45 per cent. of the theoretical and Ost (*Ber.*, 1913, **46**, 2995) recorded a yield of 50 per cent. of the theoretical from the products of hydrolysis of cellulose. In a more recent paper on the hydrolysis of cellulose by dilute mineral acid by Wohl and Blumrich (*Z. angew. Chem.*, 1921, **34**, 18),

the yield of glucosazone represented only 27 per cent. of the amount of glucose determined by other methods.

According to E. Fischer (*Ber.*, 1887, **20**, 821), the formation of phenylglucosazone by the interaction of phenylhydrazine acetate and glucose takes place in such a manner that part of the phenylhydrazine acts as an oxidising agent, converting a secondary alcohol group adjacent to the hydrazine group in glucosephenylhydrazone into a ketone group, which combines with a further molecule of phenylhydrazine. That phenylhydrazine should be reduced under these conditions to aniline and ammonia appears remarkable, seeing that its general characteristics are those of a strong reducing agent. Furthermore, phenylhydrazine is not reduced by such a powerful reducing agent as titanous chloride, although in the case of *p*-nitrophenylhydrazine reduction by this reagent has been shown to take place quantitatively to *p*-phenylenediamine and ammonia (Robinson, *J. Manchester Coll. Techn.*, 1913, **7**, 105).

For the present work, phenylglucosazone was prepared by the interaction of glucose and phenylhydrazine acetate in quantities represented empirically by the equation

$$C_6H_{12}O_6 + 3NHPh{\cdot}NH_2 = C_6H_{10}O_4(:N{\cdot}NHPh)_2 + NH_2Ph + NH_3 + 2H_2O,$$

and it was found that 1·8 grams of glucose in 100 c.c. of reacting solution gave, after three hours' heating on a water-bath, yields of osazone amounting to only 50—65 per cent. of the theoretical. Fischer (*loc. cit.*) stated that both aniline and ammonia were formed during the reaction in considerable quantity, but as no quantitative examination appears to have been carried out, an attempt has now been made to examine the filtrate from the osazone preparation for aniline, ammonia, phenylhydrazine, and glucose. This examination was, however, beset with many difficulties, the presence of both glucose and phenylhydrazine rendering copper-reduction methods impracticable, whereas the ordinary methods of estimating aniline have been found useless in presence of phenylhydrazine. If the latter is destroyed by boiling with Fehling's solution, the copper interferes with the aniline estimation.

The action of nitrous acid on phenylhydrazine was examined with a view to its possible utilisation for estimating both aniline and excess phenylhydrazine, for it had been shown by Fischer (*Annalen*, 1878, **190**, 92) and by Dimroth (*Ber.*, 1902, **35**, 1032) that nitrous acid reacts with phenylhydrazine to give phenylazoimide. But by quantitative examination it has now been found that excess nitrite, representing about 20 per cent. over and above that required to form the azoimide had to be added before an end-

point was reached. It has been found that besides phenylazoimide being formed by the reaction

$$NHPh{\cdot}NH_2 + HNO_2 \longrightarrow NO{\cdot}NPh{\cdot}NH_2 + H_2O \longrightarrow PhN_3 + 2H_2O,$$

a diazo-compound results simultaneously. By coupling with β-naphthol, benzeneazo-β-naphthol was obtained, being identified after crystallisation by its melting point. This secondary reaction, which may become the principal reaction under chosen conditions (Altschul, *J. pr. Chem.*, 1896, [ii], **54**, 496), is no doubt brought about by the oxidising action of the nitrous acid, and accounts for the excess nitrite required in the titration. This view is rendered the more probable in that Chattaway (T., 1908, **93**, 852) has shown that aromatic hydrazines are converted into diazo-compounds by chlorine. On the other hand, it has been shown that diazo-compounds are also formed by the action of nitrous acid on nitroso-compounds (O. Fischer, *Annalen*, 1889, **255**, 144; Hantzsch, *Ber.*, 1902, **35**, 894). The production of a diazo-compound by the interaction of phenylhydrazine and nitrous acid confirms the observation of Rügheimer (*Ber.*, 1900, **33**, 1718), who obtained benzenediazonium nitrate by passing nitrous oxide into a solution of nitrosophenylhydrazine in dry ether.

Owing to these complications, the use of nitrous acid was abandoned and the method adopted for the estimation of the phenylhydrazine was that described by Strache (*Monatsh.*, 1892, **13**, 299), which consists in collecting the nitrogen liberated on boiling with Fehling's solution. By this method, only free phenylhydrazine is estimated, but not any present as hydrazone. Distillation methods for estimating the ammonia were found satisfactory provided the production of tarry matters was avoided. The titration of the ammonia in the distillate was done with $N/10$-hydrochloric acid with litmus as indicator, aniline salt reacting as free acid to this indicator.

Both phenylhydrazine and *p*-nitrophenylhydrazine have been employed in this work; the glucose used was anhydrous and was found by polarimetric estimation to be of 99·1 per cent. and by copper reduction of 99·2 per cent. purity.

The result of the analytical work is given in the table on page 225.

In each set of experiments the glucose and phenylhydrazine were dissolved in a mixture of 190 c.c. of water and 10 c.c. of glacial acetic acid. The solution was heated for two hours on a water-bath, when it was allowed to cool and the osazone filtered off, dried, and weighed. The filtrate was made up to a measured volume and aliquot parts were analysed.

	Phenyl-glucosazone.	*p*-Nitrophenyl-glucosazone.
Grams of glucose taken	3·60	1·80
Grams of the hydrazine taken	6·48	4·59
Yield of osazone	3·68	3·03
Hydrazine used to form osazone (calculated) ...	3·33	3·09
Free hydrazine found in solution	2·13	1·05
Hydrazine not accounted for	1·02	0·45
Glucose not accounted for	1·75	0·585
Hydrazine required to convert the preceding quantity of glucose into hydrazone ...	1·05	0·497
Ammonia found by distillation	0·182	0·120
Ammonia calculated from yield of osazone ...	0·174	0·115

Although these results do not represent that degree of accuracy which is usually demanded in quantitative determinations, they are as good as could be expected considering the difficulties which were encountered. They sufficiently indicate, however, that the equation generally used to represent the formation of the osazone of glucose is justified. It is further inferred from the analytical data that the glucose which is not converted into the osazone is present in the solution mainly as glucosephenylhydrazone.

The yields of osazone obtained in the two quantitative experiments described above (51 and 67 per cent., respectively, of those theoretically possible) not being considered satisfactory, it was decided to ascertain whether by the choice of more suitable conditions they could not be materially increased. To this end, glucose and phenylhydrazine were caused to interact in the proportions demanded by theory and under various conditions. The time chosen in these experiments was three hours, it having been ascertained that the yield of osazone was only very slightly increased by continuing the heating for longer periods. The temperature was the same in all cases, that is, that of the water-bath, for it was found that at lower temperatures the interaction was considerably retarded, whilst at higher temperatures tarry by-products were liable to be formed.

Before these experiments were undertaken it was thought that owing to the low yield of phenylglucosazone the reaction might be of a reversible character and the effect of the addition of aniline acetate and of ammonium acetate to the reacting mixture was ascertained; instead of diminishing the yield these additions were found to increase it. On the other hand, it was found on one occasion that doubling the amount of phenylhydrazine had the effect of increasing the yield of glucosazone by about 10 per cent.

Effect of concentration on the yield.

The following quantities were employed: 3·6 grams of glucose, 6·48 grams of phenylhydrazine, and 10 c.c. of glacial acetic acid.

C.c. of solution	400	200	150	100	50
% Yield of osazone	29	45	66	78	82

Effect of acetic acid on the yield.

The quantities employed were the same as in the preceding table except in the case of the acetic acid, the amount of which was varied. The total volume was 100 c.c.

C.c. of acetic acid	2	6	10	14	20	30
% Yield of osazone	36	71	81	82	84	77

It should be noted that the diminution in the yield of osazone at high acetic acid concentration is not due to partial solubility in this acid, for the yield stated includes the slight amount obtained by diluting the acid. In the higher concentrations of acetic acid, the product was dark coloured owing to tarring.

The striking result obtained by varying the amount of acetic acid affords a possible explanation of the increased yield, alluded to above, which occurs on the addition of the acetates of aniline and ammonia to the system.

It is thus seen that although the interaction of glucose with phenylhydrazine to form phenylglucosazone did not in any case go to completion, it gave under suitable conditions yields which leave no doubt that it was the main reaction.

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MANCHESTER UNIVERSITY. [*Received, November 22nd*, 1923.]

XXX.—*Synthesis of the Higher Monoalkylmalonic Acids.*

By (MRS.) GERTRUDE MAUD ROBINSON.

AT a certain stage in the development of a synthetical investigation it became necessary to devise a convenient method of preparation of some of the less readily accessible normal fatty acids by way of the related malonic acids, none of the processes described hitherto being entirely satisfactory. As a test case, the formation of *n*-heptylmalonic acid from *n*-heptyl iodide was chosen and the values of the various methods were estimated by the extent to which the following conditions were satisfied.

(1) The yield of *n*-heptylmalonic acid calculated on the basis of the *n*-heptyl iodide employed should be maximal.

(2) The formation of di-*n*-heptylmalonic acid should be minimal.

(3) The process should be convenient in manipulation and applicable to the working up of considerable quantities of material in one operation.

After numerous trials, a technique was ultimately elaborated which reached the required standard in these respects, and proved to be applicable to other cases. A mixture of the higher alkyl iodide (1 mol.), an excess of ethyl cyanoacetate (2 mols. or more), and potassium carbonate (1·5 mols.) is boiled under reflux in a partial vacuum until the reaction is completed. The unchanged ethyl cyanoacetate is then recovered by distillation, the whole residue hydrolysed by means of aqueous sodium hydroxide (20 per cent.) on the steam-bath, and the product precipitated from the resulting solution by the addition of dilute sulphuric acid. The details of the results obtained will be found in the experimental portion, but it may be mentioned here that whereas α-cyanononoic, α-cyanodecoic, and α-cyanotridecoic acids were found to be readily hydrolysed under these conditions to related malonic acids, α-cyano-*cyclo*hexylacetic acid yielded only the malonamic acid,

$$*CH_2\begin{<}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{>}CH\cdot CH(CO\cdot NH_2)\cdot CO_2H,$$

which is remarkably resistant to hydrolysis by means of alkali in both aqueous and alcoholic solutions. The phenomenon may be due to steric hindrance, because if a boat-shaped configuration of the ring may be assumed, it is obvious that in one conceivable arrangement of the atoms of the side chain the positions in space of the amino-group and of the methylene group denoted by an asterisk are approximately coincident.

Experimental.

cyclo*Hexylmalonamic Acid.*—A mixture of *cyclo*hexyl iodide (25 grams), ethyl cyanoacetate (27 grams), and potassium carbonate (13 grams) was boiled under 60 mm. pressure by heating in an oil-bath at 140° during one hour, 150–160° during five hours, and finally at 160—170° for half an hour. After removal of the excess ethyl cyanoacetate by distillation in a vacuum, the residue was heated on the steam-bath with aqueous sodium hydroxide (60 c.c. of 20 per cent.) during two and a half hours, when a sodium salt separated and after cooling was collected. On treatment with dilute sulphuric acid, the corresponding acid was obtained, and this was collected and dried (11·5 grams). A further quantity (2·0 grams) was obtained by acidification of the alkaline solution, the total yield being 62 per cent. of that demanded by theory. Hope and Perkin condensed *cyclo*hexyl bromide and the sodium

derivative of ethyl malonate in alcoholic solution and found the yield of ethyl *cyclo*hexylmalonate amounted to 33 per cent. of the theoretical (T., 1909, **95**, 1363).

cyclo*Hexylmalonamic acid* crystallises well from formic acid in colourless needles, m. p. 184° (Found: C = 58·5; H = 8·2. $C_9H_{15}O_3N$ requires C = 58·4; H = 8·1 per cent.). When a solution of this acid (4·0 grams) in ethyl alcohol (20 c.c.) and water (5 c.c.) containing potassium hydroxide (6·0 grams) was heated on the steam-bath during four hours, no ammonia was evolved and the unchanged substance was recovered. On heating in a tube, the acid decomposes with evolution of carbon dioxide and a snowy sublimate is formed. The substance crystallises from aqueous alcohol in elongated plates, m. p. 168° (Found: C = 68·2; H = 10·6. Calc. for $C_8H_{15}ON$, C = 68·1; H = 10·6 per cent.). Wallach (*Annalen*, 1907, **353**, 284) states that *cyclo*hexylacetamide melts at 168°.

n-*Heptylmalonic Acid.*—In this case, various methods were employed and the following was found to give the best results. A mixture of ethyl cyanoacetate (13·5 grams), *n*-heptyl iodide (9·0 grams), and potassium carbonate (4·5 grams) was vigorously boiled under reflux (18 mm. pressure, oil-bath at 140—150°) during four hours and then during an hour with the oil-bath at 150—160°. After removal of the excess of ethyl cyanoacetate, the residue was hydrolysed at 100° by means of aqueous sodium hydroxide (50 c.c. of 20 per cent.) during five hours. The oil obtained on acidification rapidly solidified and was collected, washed with water, and dried (6·7 grams). This is a yield of 84 per cent. of the theoretical, but a further quantity remains in the solution, since, contrary to the statement of Piccinini (*Atti R. Acad. Sci. Torino*, 1903, **39**, 20), the acid is appreciably soluble in water. The crude product is practically pure and on crystallisation from a mixture of benzene and light petroleum is obtained in colourless, rhombic prisms melting at 95°, which is the melting point recorded by Piccinini (*loc. cit.*). On distillation, pelargonic acid was formed, and this was identified as the zinc salt, which crystallised from alcohol in rosettes of needles melting at 131—132°, alone or mixed with zinc pelargonate.

n-*Octylmalonic Acid.*—The proportions employed in the preparation of this acid from *n*-octyl iodide were similar to those used in the preceding experiment. The pressure was 14 mm. and the oil-bath was maintained at 120° during half an hour and then at 160—167° during eight hours. The yield was 95 per cent. of the theoretical. The acid crystallises from benzene containing a little light petroleum in colourless, flat prisms or from chloroform in

rhombic prisms, m. p. 115° (Found : C = 61·3; H = 8·9. $C_{11}H_{20}O_4$ requires C = 61·1; H = 9·2 per cent.).

The acid is mentioned by Smith (*Z. physikal. Chem.*, 1898, **25**, 193), but no analysis or description appears to have been recorded. On distillation it yields decoic acid, m. p. 31°, alone or mixed with a specimen of the substance derived from natural sources. Octylmalonic acid is unaffected by prolonged treatment in the cold with a concentrated solution of potassium hypobromite or with bromine water.

n-*Undecylmalonic Acid.*—*n*-Undecyl alcohol, *n*-undecyl iodide, ethyl *n*-undecylmalonate, and *n*-undecylmalonic acid have been prepared by Levene, West, Allen, and Van der Scheer (*J. Biol. Chem.*, 1915, **23**, 71), but the yield of the malonic derivative is not cited. A quantitative yield of methyl undecoate of negligible iodine value was obtained by the reduction of methyl undecylenate with hydrogen and a nickel catalyst, and the author is indebted to Dr. Salway and Messrs. Lever Brothers, who kindly undertook the preparation in their experimental plant. The ester was reduced to *n*-undecyl alcohol by the Bouveault method, which was also employed by the authors quoted above, who obtained 23 grams of the alcohol from 50 grams of the ester. The following modification gives better results. To sodium (30 grams), cut in large pieces and heated by an oil-bath at 140°, a mixture of methyl undecoate (30 grams) and thoroughly dried ethyl alcohol (100 c.c.) was added during thirty minutes, the temperature meanwhile being gradually raised to 170°. After one hour, dry ethyl alcohol (50 c.c.) was added, and the heating continued during three further hours. The yield of pure *n*-undecyl alcohol, b. p. 130°/12 mm., m. p. 14·3°, was 21·5 grams, which is 83 per cent. of the theoretical. The action of red phosphorus and iodine on the alcohol gave *n*-undecyl iodide, b. p. 155°/13 mm., in a yield of 85 per cent. of the theory and an iodine estimation showed that the product contained 98·5 per cent. of the pure substance. *n*-Undecyl iodide was found to react with activated magnesium in presence of ether in the normal manner. It was reduced by means of aluminium amalgam in boiling alcoholic solution with formation of *n*-undecane, b. p. 195°, and a relatively small amount of docosane, $C_{22}H_{46}$, which crystallises from toluene in plates, m. p. 44·5°. For comparison the latter substance was also prepared by the action of sodium on a boiling solution of *n*-undecyl iodide in toluene containing 5 per cent. of its volume of *iso*amyl ether. The product was the same hydrocarbon boiling at 327°/768 mm. and melting at 44·5°. *n*-Undecane has previously been obtained by Krafft (*Ber.*, 1882, **15**, 1697) by the reduction of *n*-undecoyl chloride with hydriodic acid and

phosphorus, whilst Schall (*Ber.*, 1892, **25**, 1489) found that it was one of the constituents of an oil obtained from ants. *n*-Docosane is one of the products of the distillation of brown coal and has been prepared by the reduction in stages of *n*-pentadecyl *n*-hexyl ketone (Krafft, *Ber.*, 1882, **15**, 1712).

A mixture of *n*-undecyl iodide (9·0 grams), ethyl cyanoacetate (7·8 grams), and potassium carbonate (3·0 grams) was heated at 150° under 14 mm. pressure during six hours. After removal of the unchanged ethyl cyanoacetate, the residue was hydrolysed during four hours by means of aqueous sodium hydroxide (50 c.c. of 20 per cent.) at 100°. On acidification of the solution, *n*-undecylmalonic acid was precipitated and after collection and drying weighed 6·5 grams, which is a yield of 81 per cent. of the theoretical. The acid crystallises from chloroform in rectangular needles, m. p. 108° (Found: C = 65·2; H = 9·9. $C_{14}H_{21}O_4$ requires C = 65·1; H = 10·1 per cent.). On distillation a 91 per cent. yield of tridecoic acid, m. p. 43°, was obtained. Zinc tridecoate crystallises from *iso*amyl alcohol in clusters of needles, m. p. 128°. It is sparingly soluble in boiling ethyl alcohol.

n-*Hexadecylmalonic Acid.*—Hexadecyl iodide (6·0 grams), m. p. 22°, was heated with ethyl cyanoacetate (3·5 grams) and potassium carbonate (2·5 grams) at 170—180° under 20 mm. pressure during four hours. The product was hydrolysed during twenty-two hours by means of boiling 25 per cent. aqueous potassium hydroxide. The yield was 4·8 grams, or 90 per cent. of the theoretical. The substance was crystallised from acetone, alcohol, and high-boiling petroleum and obtained in colourless needles, m. p. 119° (Guthzeit, *Annalen*, 1881, **206**, 359, gives 117° and Hell and Sadomsky, *Ber.*, 1891, **24**, 2781, give 121—122° as the melting point). On heating at 140—150°, the acid decomposed with formation of stearic acid, which was crystallised from acetone and then from alcohol and melted at 69°, alone or mixed with stearic acid.

n-*Decyldimethylcarbinol.*—Magnesium (11 grams) was brought into reaction with methyl iodide (2·0 grams) and a little ether, and a further quantity of dry ether (160 c.c.) added. A solution of methyl undecoate (40·8 grams) and methyl iodide (58 grams) in dry ether (250 c.c.) was then introduced through the reflux condenser at such a rate as to keep the reaction moderately vigorous. Ether (30 c.c.) was used to wash down the condenser and when the action slackened the mixture was gently boiled during one hour. The alcohol was isolated in the usual manner, any unchanged ester being removed from the product by hydrolysis with methyl-alcoholic potassium hydroxide. Finally, 36 grams of a pleasant smelling, mobile oil, b. p. 145°/10 mm., were isolated, the

yield being 88 per cent. of the theoretical (Found: C = 77·8; H = 14·2. $C_{13}H_{28}O$ requires C = 78·0; H = 14·0 per cent.).

Grateful acknowledgment is made to the Food Investigation Board of the Department of Scientific and Industrial Research for a grant which has facilitated this investigation.

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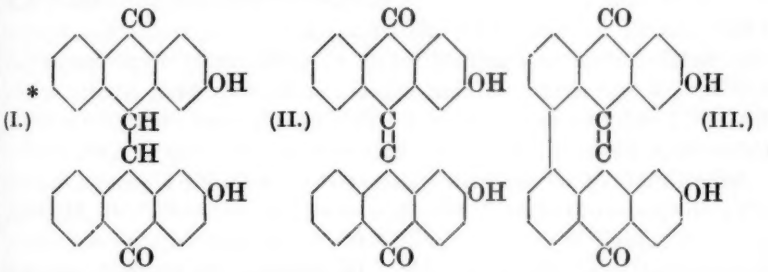
XXXI.—*Reduction Products of the Hydroxyanthraquinones. Part IV.*

By JOHN WALTER ECROYD HALLER and ARTHUR GEORGE PERKIN.

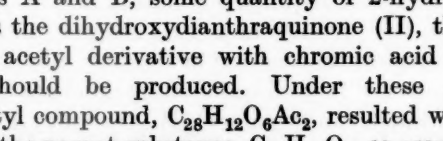
IT was shown by Bradshaw and Perkin (T., 1922, **121**, 1911) that when 2-hydroxyanthraquinone is heated at 170—180° with glucose and alkali in the presence of a little sodium nitrate, in addition to 2-hydroxybenzanthronecarboxylic acid, the main crystalline product, there are formed quite small amounts of two compounds A and B, to which the formulæ $C_{28}H_{16}O_4$ and $C_{28}H_{14}O_4$, respectively, were provisionally assigned. From A, which is distinguished by the violet colour of its sulphuric acid solution, diacetyl and dimethyl derivatives were prepared, whereas of B, the sulphuric acid solution of which is red, sufficient was only available for a preliminary study of the acetyl derivative. Again, Perkin and Whattam (T., 1922, **121**, 297) obtained A, although only in small amount, by the oxidation of the dihydroxydianthrone (I) with alkaline permanganate, and it has now been ascertained that, as a rule, a trace of B is simultaneously produced by this method. It thus appeared likely that A was 3 : 3′-dihydroxydianthraquinone (II) and that compound B, with which it is evidently closely allied, was the corresponding helianthrone (III).



* The hydroxyl groups may obviously be present either in the 3 : 3′ or the 3 : 6′ positions.

The preparation of A and B in quantity by the glucose–alkali method being out of the question, the oxidation of the dihydroxydianthrone with permanganate was further studied, but again, curiously enough, a yield of A higher than 10 per cent. could not be obtained. Employing potassium ferricyanide, however, the results were better, and eventually a 99 per cent. yield of the crude substance A, accompanied by a small amount of B, was obtained in this way. It was observed that these two substances can also be obtained from 3-hydroxyanthranol itself by oxidation with ferricyanide, although in a smaller amount than when the dihydroxydianthrone is used. This difference in yield is apparently due to the fact that the 2-hydroxyanthranols are much more readily oxidised to the hydroxyanthraquinones in alkaline solution, than are the hydroxydianthranols. Thus when alkaline ferricyanide is used it has been found that 3-hydroxyanthranol yields, in addition to the substances A and B, some quantity of 2-hydroxyanthraquinone. If A is the dihydroxydianthraquinone (II), then by the oxidation of its acetyl derivative with chromic acid 2-acetoxyanthraquinone should be produced. Under these conditions, however, a diacetyl compound, $C_{28}H_{12}O_6Ac_2$, resulted which, when hydrolysed, gave the parent substance, $C_{28}H_{14}O_6$, as orange needles. This compound, which also yields a dimethyl ether, $C_{28}H_{12}O_4(OMe)_2$, is evidently the dihydroxy-1 : 1′-dianthraquinonyl (IV) which, for the reasons given below, with little doubt contains the hydroxyl groups in the 2 : 7′ positions.

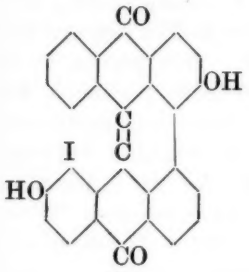
(IV.)



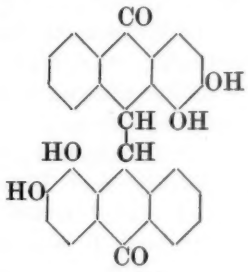
It thus follows that compound A is a 3 : 6′-dihydroxyhelianthrone, $C_{28}H_{14}O_4$ (III), and not the dihydroxydianthraquinone, $C_{28}H_{16}O_4$ (II), as was at first considered to be probable. Scholl (*Ber.*, 1910, **43**, 1734) has shown that 1 : 1′-dianthraquinonyl on reduction passes into helianthrone and as the result of preliminary experiments it has been found that a similar change, at least in part, occurs when the 2 : 7′-dihydroxy-compound (IV) is digested with stannous chloride in hydrochloric acid solution at the boiling temperature.

When diacetylhelianthrone is treated in boiling pyridine solution with an excess of iodine it gives the monoiodo-derivative, $C_{28}H_{13}O_4I$, which is soluble in sulphuric acid with a cornflower-blue coloration. The formation of this substance is of considerable interest because of the evidence it affords that the hydroxyl groups present in this dihydroxyhelianthrone occupy the 3 : 6′ positions.

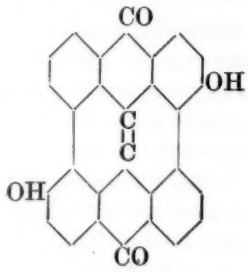
There can be little doubt that the iodine has entered this compound in the α-position adjacent to a hydroxyl group, and that as a result only one such position in the original dihydroxy-compound can thus be free. If the substance was a 3 : 3′-dihydroxyhelianthrone (III), it might be expected to yield a di-iodo-derivative under the conditions employed, but as there has been no evidence of the production of such a compound, the hydroxyl groups must be assumed to occupy the 3 : 6′ positions, and the iodine of the iodo-compound position 5′ (V). It would thus appear that the dihydroxy-



(V.)



(VI.)



(VII.)

dianthrone (I) from which this dihydroxyhelianthrone is prepared by oxidation reacts as a 3 : 6′-dihydroxy-compound, and this orientation may be the general rule in respect of the hydroxydianthrones derived from hydroxyanthranols containing hydroxyl groups in the 3 and 4 positions, or both. If this is the case, the dianthrone from deoxyalizarin is to be represented as the 3 : 4 : 5′ : 6′-compound (VI), and this view would account for the failure of all attempts made in this laboratory to convert it into a tetrahydroxyhelianthrone.

3 : 6′-Dihydroxyhelianthrone yields sparingly soluble, orange-red alkali salts which, with alkaline hyposulphite, give a bluish-green solution. The vats obtained in this way dye cotton a bluish-green colour which rapidly passes through red to orange on exposure to air. In this and other respects, 3 : 6′-dihydroxyhelianthrone resembles the 4 : 4′-dihydroxyhelianthrone of Scholl and Seer (*Ber.*, 1911, **40**, 1091), which gives a green vat, from which cotton can be dyed an orange-red shade. 3 : 6′-Dihydroxyhelianthrone, in the colloidal condition, possesses adjective dyeing property, and gives, with wool mordanted with chromium, a dull orange shade.

A further examination of the substance B, which appears to be always associated to a small extent with the 3 : 6′-dihydroxyhelianthrone prepared according to the methods described in this communication, indicates that this substance is $C_{28}H_{10}O_2(OH)_2$

and therefore that it contains two hydrogen atoms less than 3 : 6′-dihydroxyhelianthrone. Such a formula corresponds with that of a dihydroxy*meso*naphthadianthrone. It has been shown by Scholl (*Ber.*, 1919, **52**, 829) and by Meyer, Bondy, and Eckert (*Monatsh.*, 1912, **33**, 1451) that helianthrone can be readily converted into naphthadianthrone and again (Eckert and Tomaschek, *Monatsh.*, 1918, **39**, 839) that halogen derivatives of helianthrone readily undergo a similar change. As an attempted conversion of 3 : 6′-dihydroxyhelianthrone into compound B by oxidation with ferricyanide was unsuccessful, a result possibly due to the sparing solubility of this substance in alkali, the method of Scholl, which involves the use of aluminium chloride, was studied. This proved to be effective, some quantity of the substance (B) being produced, but a better result was obtained on exposing the benzene or acetic acid solution of the 3 : 6′-diacetoxyhelianthrone to sunlight for some weeks (compare Meyer, Bondy, and Eckert, *loc. cit.*), when an almost quantitative yield of acetyl B was thus obtained. There can be no doubt, therefore, that B is in reality 3 : 6′-dihydroxy-*meso*naphthadianthrone (VII). This compound appears to yield an oxonium sulphate and gives alkali salts almost insoluble in water. It resembles *meso*naphthadianthrone itself in that it does not yield a vat with sodium hyposulphite alone.

In order to account for formation of 3 : 6′-dihydroxyhelianthrone and naphthadianthrone during the fusion of 2-hydroxyanthraquinone with alkali and glucose in the presence of a little sodium nitrate, it seems probable that the oxidising effect of the latter does not come fully into play until the alkaline glucose reduction has ceased. Probably 3-hydroxyanthranol is first produced and this is then partly converted into 2-hydroxybenzanthronecarboxylic acid, as described in the earlier paper (*loc. cit.*). Oxidation of the unattacked 3-hydroxyanthranol to the dianthranol will then presumably occur, followed by the production therefrom of the dihydroxyhelianthrone and naphthadianthrone. In the absence of the nitrate these two substances are not formed.

It is natural to suppose that the formation of dihydroxyhelianthrone and naphthadianthrone from the dihydroxydianthrone is preceded by that of the dihydroxydianthraquinone (II). This actually appears to be the case to some extent, because during the oxidation of 3 : 6′-dihydroxydianthrone in alkaline solution with the theoretical amount of ferricyanide required for this change, a product, soluble in sulphuric acid with a brown colour, is produced. When the crude acetyl derivative obtained from this product is submitted to fractional crystallisation, the less soluble portion dissolves in boiling acetic anhydride with a deep green tint, and

in sulphuric acid with a dull maroon colour, reactions characteristic of dianthraquinone itself. Oxidation with chromic acid converts this acetyl compound into 2-acetoxyanthraquinone, and it thus appears to consist, mainly at least, of 3 : 6′-diacetoxydianthraquinone. This substance has hitherto been difficult to obtain in sufficient amount for full investigation, and work is now in progress with the object of devising methods more suitable for its preparation, in a pure condition.

Experimental.

Perkin and Whattam (*loc. cit.*) obtained 3 : 6′-dihydroxydianthrone by the oxidation of 3-hydroxyanthranol or its acetyl compound with ferric chloride in boiling acetic acid. The reaction, however, proceeds better in the presence of sodium acetate. The proportions employed in this investigation have been 3-hydroxyanthranol (5 grams), acetic acid (50 c.c.), sodium acetate (4·5 grams), and commercial ferric chloride (6·7 grams) in acetic acid (7 c.c.). 4·4 Grams of the dianthrone thus separate on the average, and from the filtrate, by dilution with water, 0·4 gram can also be isolated, corresponding to a yield of 96 per cent. After digestion with boiling acetone or boiling acetic acid to remove a trace of unattacked 3-hydroxyanthranol, the product was practically pure.

Oxidation of the Dianthrone.—In the former communication no details of the permanganate method are given, whereas certain of these are now found to be of importance. 3 : 6′-Dihydroxydianthrone (0·5 gram) in a slight excess of sodium hydroxide solution (10 per cent.) was treated with 2 per cent. permanganate solution (6·3 c.c.). After ten minutes, the mixture was slowly heated to the boiling point, kept there for ten minutes longer, oxalic acid added, and the brown precipitate collected and dried. From this, by repeated extraction with small quantities of boiling acetone, a residue (0·05 gram) of nearly pure substance A, soluble in sulphuric acid with a violet coloration, was obtained.

As other experiments by this method failed to improve the yield, the employment of alkaline ferricyanide was studied and the following process eventually adopted. To a solution of dihydroxydianthrone (10 grams) in 10 per cent. sodium hydroxide * (120 c.c.), cooled by ice, 20 per cent. potassium ferricyanide solution (160 c.c.; the theoretical amount) was added during ten minutes. After two hours, the well-cooled mixture was acidified with dilute hydrochloric acid and the precipitate collected. The yield was

* Before cooling, the alkaline solution of the dihydroxydianthrone is raised to the boiling point. Thus for the success of the reaction a conversion of the dihydroxydianthrone into dihydroxyanthranol appears to be essential.

9·9 grams, and a preliminary purification of the product, by means of acetone, was unnecessary.

Complete purification was best effected by the preparation of the acetyl derivative, and from this a trace of acetyl (B) could be removed by means of its sparing solubility in benzene (Bradshaw and Perkin, *loc. cit.*) (yield 6·5 grams). The melting point 275—277° previously given for this compound (acetyl A) was confirmed (Found: C = 77·33; H = 3·4. Calc. for $C_{32}H_{18}O_6$, C = 77·17; H = 3·61 per cent.).

Oxidation of 3-Hydroxyanthranol.—3-Hydroxyanthranol (10 grams) in 10 per cent. sodium hydroxide solution (150 c.c.), cooled by ice, was treated with 20 per cent. ferricyanide solution (80 c.c.), and the mixture heated on the water-bath. To the well-cooled liquid a further 160 c.c. of the ferricyanide solution were now added, and after keeping for two hours the product was acidified. From the reddish-brown powder (9·8 grams) boiling acetone removed a brown impurity, and eventually a residue of A (4·8 grams), soluble in sulphuric acid with a pure violet colour, was isolated. The acetone extract, by fractional evaporation, deposited first a trace of A, and subsequently a yellowish-brown, crystalline product. This on acetylation gave an acetyl compound melting at 159°, identical with 2-acetoxyanthraquinone.

2 : 7′-*Dihydroxy*-1 : 1′-*dianthraquinonyl.*—The acetyl compound of (A) (0·8 gram), dissolved in boiling acetic acid, was treated with pure chromic acid (0·5 gram), little by little, and the digestion continued until the presence of the latter was no longer evident. Cautious addition of boiling water caused the separation of bright yellow crystals, 0·67 gram, which, after recrystallisation from acetic anhydride, consisted of small plates, m. p. 277° (Found: C = 72·29; H = 3·6. $C_{32}H_{18}O_8$ requires C = 72·45; H = 3·4 per cent.). This acetyl derivative, by treatment with sulphuric acid in boiling acetic acid solution, yielded a blood-red liquid, and this by gradual addition of boiling water deposited minute, orange-yellow needles. The yield was 83·50 per cent., whereas the theory for the loss of two acetyl groups is 84·1 per cent. 2 : 7′-Dihydroxy-1 : 1′-dianthraquinonyl crystallises from nitrobenzene in small prisms or leaflets and is soluble in dilute alkalis with a crimson colour (Found: C = 75·25; H = 3·14. $C_{28}H_{14}O_6$ requires C = 75·30; H = 3·13 per cent.). It dissolves in sulphuric acid to form a bright scarlet solution which in daylight becomes first crimson, then violet, and finally violet black.* It does not melt below 350°.

A suspension of 2 : 7′-dihydroxydianthraquinonyl in methyl

* In the dark or in ordinary artificial light these colour changes do not occur.

alcohol was methylated by repeated treatment with equivalent amounts of methyl sulphate and alkali. On addition of water a crystalline powder separated, which was washed with dilute alkali and recrystallised from much acetic acid. It was thus obtained as small, yellow prisms, m. p. about 343—344° (Found : C = 75·85; H = 3·98. $C_{30}H_{18}O_6$ requires C = 75·9; H = 3·77 per cent.).

2 : 7′-*Dimethoxy*-1 : 1′-*dianthraquinonyl* is soluble in sulphuric acid with a scarlet colour.

A mixture of 2 : 7′-diacetyldianthraquinonyl (0·2 gram), stannous chloride (2 grams), and hydrochloric acid (10 c.c.) was digested at the boiling point for three hours, yielding a dark brown powder, soluble in sulphuric acid with a dull green tint. After acetylation with acetic anhydride and pyridine, the solution deposited, on cooling, a brownish-violet precipitate, which was removed, and the filtrate then treated with water. The dull coloured deposit thus obtained, when dry, dissolved in sulphuric acid with a bright violet coloration, and consisted, with little doubt, mainly of 3 : 6′-diacetoxyhelianthrone.

5-*Iodo*-3 : 6′-*dihydroxyhelianthrone*.—3 : 6′-Diacetoxyhelianthrone (1 gram) was dissolved in hot pyridine (15 c.c.), iodine (1·5 grams) added, and the dull red solution boiled for two minutes, kept for half an hour, and then poured into a freshly acidified solution of sodium bisulphite. The brick-red precipitate was well washed, dried (the yield was 107·6 per cent., whereas the theory for the production of mono-iodo-compound is 108 per cent.), and digested with a little boiling acetic anhydride, containing pyridine. As the reaction proceeded, crystals separated, which were collected, and dissolved in much benzene. On evaporation to a small bulk, the acetyl compound was obtained in minute, glistening, orange-yellow needles, m. p. 282° (Found : C = 61·8; H = 2·8; I = 20·77. $C_{32}H_{17}O_6I$ requires C = 61·5; H = 2·7; I = 20·35 per cent.).

5-Iodo-3 : 6′-diacetoxyhelianthrone (0·5715 gram) was only hydrolysed with difficulty by means of sulphuric acid (2 c.c.) in boiling glacial acetic acid suspension (20 c.c.), slight decomposition occurring. The dull brick-red powder (yield 87·3 per cent.; theory for the loss of two acetyl groups = 86·54 per cent.) was treated with a little cold diethylamine, the liquid diluted with alcohol and filtered from a trace of unattacked acetyl compound. The liquid was heated to boiling and at once acidified, and on continued digestion a scarlet powder, consisting of extremely fine needles, separated. Dihydroxyiodohelianthrone does not melt below 350°, dissolves sparingly in hot dilute alkali with a red, and in sulphuric acid with a cornflower-blue colour. Alkaline hyposulphite yields a deep green vat which dyes cotton a green shade. This changes

to scarlet in air, and becomes slightly yellower in tone when washed with dilute acid.

3 : 6′-*Dihydroxynaphthadianthrone* (VII).—This compound (B), which is in most cases obtained simultaneously with 3 : 6′-dihydroxyhelianthrone in trifling amount by the methods given above, is distinguished by yielding an acetyl compound very sparingly soluble in boiling benzene, whereas the acetoxyhelianthrone is thus somewhat readily dissolved. The acetyl compound thus isolated was recrystallised from nitrobenzene (Found: C = 77·43; H = 3·34. $C_{32}H_{16}O_6$ requires C = 77·3; H = 3·2 per cent.). It consists of faintly yellow needles which darken at about 300° and become black without melting at 350°.

0·4279 Gram in boiling acetic acid (15 c.c.) was treated with sulphuric acid (2·5 c.c.), causing the gradual formation of a microcrystalline, maroon-coloured paste, probably an oxonium sulphate. This, by cautious addition of boiling water, was transformed into an orange-brown powder, of a semi-crystalline character (0·3555 gram) (Found: $C_{28}H_{12}O_4$ = 83·05. $C_{32}H_{16}O_6$ requires $C_{28}H_{12}O_4$ = 83·06 per cent.). The 3 : 6′-dihydroxynaphthadianthrone thus obtained is almost insoluble in nitrobenzene, dissolves sparingly in pyridine, and does not melt below 350° (Found: C = 81·37; H = 3·01. $C_{28}H_{12}O_4$ requires C = 81·5; H = 2·7 per cent.). Its sulphuric acid solution is crimson in colour, whereas with sodium hydroxide it yields a red sodium salt almost insoluble in water. The latter becomes somewhat lighter in colour in contact with alkaline hyposulphite solution, but does not dissolve, and thus resembles *meso*naphthadianthrone itself (Scholl, *Ber.*, 1919, **52**, 1829). The diacetoxy-compound, by treatment with chromic acid in acetic acid solution, is gradually broken down into water-soluble products. Thus 0·1 gram, suspended in acetic acid (6 c.c.), and digested at the boiling point with chromic acid (0·2 gram) for half an hour, yielded 0·06 gram of unchanged substance, whereas the filtrate gave no precipitate on dilution with water.

Conversion of 3 : 6′-*Dihydroxyhelianthrone into* 3 : 6′-*Dihydroxynaphthadianthrone.*—Diacetoxyhelianthrone (0·5 gram) was ground with aluminium chloride (3 grams) (Scholl, *loc. cit.*), and the mixture heated at 140° to 160° for one hour. The product was stirred with hydrochloric acid and treated with water, the precipitate collected, and when dry, digested with acetic anhydride and pyridine. To the hot liquid a little alcohol was added, some quantity of an amorphous precipitate removed, and the filtrate further diluted with alcohol. After keeping, the pale yellow, crystalline precipitate was collected and recrystallised from nitrobenzene. It dissolved in sulphuric acid with a crimson colour,

had not melted at 350°, and had all the properties of 3 : 6′-diacetoxynaphthadianthrone. The yield was poor and better results were obtained as follows.

Solutions of 3 : 6′-diacetoxyhelianthrone, 1 gram in acetic acid (200 c.c.), and 0·5 gram in benzene (100 c.c.), were exposed in stoppered cylinders to daylight for about six weeks. From the solutions, which were now devoid of fluorescence, crystals had separated in considerable amount in each case, and these were soluble in sulphuric acid with a crimson colour. A complete conversion of the acetoxyhelianthrone had evidently thus occurred. The diacetylnaphthadianthrone was recrystallised from nitrobenzene and was found to be identical with that described above (Found : C = 77·15; H = 3·3. Calc. for $C_{32}H_{16}O_6$, C = 77·3; H = 3·2 per cent.).

Limited Oxidation of 3 : 6′-*Dihydroxydianthrone.*—A solution of dihydroxydianthrone (2·5 grams) in hot 5 per cent. sodium hydroxide (60 c.c.) was cooled by ice and 8 per cent. potassium ferricyanide solution (50 c.c.) gradually added during ten minutes. After keeping for a quarter of an hour, acidification gave 2·3 grams of a brown powder, and this was digested for fifteen minutes with boiling acetic anhydride (15 c.c.) containing a trace of pyridine. A yellow, crystalline product gradually separated from the boiling solution, and when cold, this was collected, washed with acetic acid, and finally with alcohol * (yield 1 gram). Recrystallisation from benzene gave yellow needles which darkened at about 270° and melted at 276—278° (Found : C = 76·59; H = 4·16. $C_{32}H_{20}O_6$ requires C = 76·8; H = 4·00 per cent.). That this compound, the absolute purity of which has not yet been established, consists in the main part of 3 : 6′-diacetoxydianthraquinone seems evident from its reactions. Thus it is sparingly soluble in boiling acetic anhydride with a bright green, and in sulphuric acid with a dull maroon tint, colour changes which in these circumstances are exhibited by dianthraquinone itself. By means of chromic acid in boiling glacial acetic acid solution a clear liquid resulted and this, on dilution with hot water, deposited crystals of 2-acetoxyanthraquinone, m. p. 157—159°. Finally, a solution of the free compound in 5 per cent. sodium hydroxide gave on treatment with potassium ferricyanide a red deposit, which was soluble in sulphuric acid with a violet coloration and evidently consisted of the sodium salt of 3 : 6′-dihydroxyhelianthrone.

* In the filtrate some quantity of 3 : 6′-diacetoxyhelianthrone was present.

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XXXII.—*Estimation of Ferrocyanides.*

By William Murdoch Cumming.

Various methods have been suggested for the estimation of ferrocyanides in solution. One difficulty attached to these has been the fact that the compound precipitated is not always that which should be precipitated according to theory. For example, in the method in which the ferrocyanide is converted into Prussian blue, with sodium and potassium ferrocyanides the compounds precipitated are $3Fe_4[Fe(CN)_6]_3$,$FeNaFe(CN)_6$ and $2Fe_4[Fe(CN)_6]_3$,$FeKFe(CN)_6$, respectively. These two examples represent errors of 1·5 and 2 per cent., respectively, in the estimation of the ferrocyanide. Moreover, the Prussian blue should be precipitated by a boiling solution of a ferric salt in concentrated sulphuric or hydrochloric acid in order to diminish the quantity of ferric hydroxide brought down with the colloidal blue precipitate. A copper salt in presence of excess of the potassium salt precipitates $Cu_6K_8[Fe(CN)_6]_5$ instead of $Cu_2Fe(CN)_6$; if the potassium salt be not in excess, $Cu_4K_4[Fe(CN)_6]_3$ and $Cu_3K_2[Fe(CN)_6]_2$ may be precipitated. Zinc sulphate gives a precipitate of $Zn_3K_2[Fe(CN)_6]_2$ with potassium ferrocyanide. The errors thus introduced render these methods quite unsuitable for the analysis of the organic hydroferrocyanides.

Other methods give accurate results only with certain salts; moreover, the precipitating solution must be standardised against the ferrocyanide to be estimated. For example, copper sulphate gives accurate results only for calcium and sodium ferrocyanides unless special precautions are taken. In all these methods care must be taken to carry out the standardisation and the estimation under exactly the same conditions in order to obtain concordant results. Williams's method (*J. Soc. Chem. Ind.*, 1912, **31**, 468) was found to give discordant results in presence of organic matter.

The author's work on the hydroferrocyanides and hydroferricyanides of the organic bases (T., 1922, **121**, 1287; 1923, **123**, 2457) has led to a simple and trustworthy method which is equally applicable to the estimation of sodium, potassium, or calcium ferrocyanide. It is based on the fact that these ferrocyanides precipitate from a neutral solution of a benzidine salt the same benzidine hydroferrocyanide, $3C_{12}H_{12}N_2,H_4Fe(CN)_6,H_2O$ (Found: Fe = 7·12, 7·14, and 7·12 in the three cases. Calc., Fe = 7·12 per cent.), the solubility of which in water at 17° is 1 part in 12,000 parts.

Gravimetric Method.—The method adopted was to add to the cold neutral solution of the ferrocyanide (0·5—1 gram) excess of benzidine hydrochloride solution (the solubility of benzidine dihydrochloride

at 17° is 0·808 gram in 100 c.c. of water). The white precipitate was filtered off, washed with water, dried in an air-bath, and ignited and the residue of ferric oxide weighed. The factors used, in testing the method, for converting the found weight of Fe_2O_3 into weight of anhydrous original salt were 4·599, 3·799, and 3·649 respectively for potassium, sodium, and calcium ferrocyanides. The results were: $K_4Fe(CN)_6,3H_2O$ contained 86·81, 87·56 (theo. 87·19) per cent. of $K_4Fe(CN)_6$; $Na_4Fe(CN)_6$, $10H_2O$ contained 62·86, 62·90 (theo. 62·81) per cent. of $Na_4Fe(CN)_6$; and crystallised calcium ferrocyanide contained 59·34, 59·67 per cent. of $Ca_2Fe(CN)_6$ [Theo. for $Ca_2Fe(CN)_6,11H_2O$, 59·59 per cent.].

With regard to the last-named salt, there has been some uncertainty as to its degree of hydration; compare Roscoe and Schorlemmer ("Treatise on Chemistry," 1913, Vol. II, p. 1256), Ewan (Thorpe's "Dictionary of Applied Chemistry," Vol. II, p. 186), and Colman (*Analyst*, 1910, **35**, 299), where $11\frac{1}{2}$ to $12H_2O$ are ascribed to the salt. Berkeley, Hartley, and Burton (*Phil. Trans.*, 1908, **209**, 180), however, assigned a formula in agreement with that now found, namely, $Ca_2Fe(CN)_6,11H_2O$.

This salt was here prepared by adding a little alcohol to a stirred, not too concentrated aqueous solution at −18°; it formed pale yellow, rhombohedral crystals stable at the ordinary temperature. It lost less than 0·5 per cent. of its weight when heated for four hours at 40—45°, and 38·70 per cent. when heated for one hour at 100° (Theo. for $10\frac{1}{2}H_2O$, 38·57 per cent.); the weight thereafter remained constant. The dehydrated salt was white with a blue tinge, was slightly hygroscopic, and, on heating at higher temperatures, gave off hydrogen cyanide. The original salt was partly dehydrated on standing for some hours over calcium chloride. An attempt was made to estimate the total water and hydrogen cyanide by heating at high temperatures in an atmosphere of dry air, but it was found that under these conditions carbon dioxide also was evolved and the residue consisted apparently of red ferric oxide and lime. In order to prevent this decomposition, the dehydration was carried out in an atmosphere of dry nitrogen and the water and hydrogen cyanide evolved were absorbed in pumice–sulphuric acid and caustic potash, respectively. The residue after ignition was greyish-white.

The following equation probably represents the change which takes place when the salt is heated above 100° in an oxgyen-free atmosphere:

$$2Ca_2Fe(CN)_6,11H_2O = Ca_4Fe_2(CN)_{11}\cdot OH + 21H_2O + HCN$$

(Found: $H_2O = 38·80$; $HCN = 2·77$. Calc., $H_2O = 38·57$; $HCN = 2·75$ per cent.). Since 1 mol. of HCN is equivalent to

1 mol. of H_2O, the total H_2O + HCN, calculated as H_2O, is 40·64 per cent. (Theo. for $11H_2O$ = 40·41 per cent.). Had the total H_2O and HCN been reckoned as H_2O, the result, 41·57 per cent., would have agreed with Colman's analysis for $11\frac{1}{2}H_2O$ (theo. 41·48 per cent.). The residue remaining was soluble in warm water, gave a blue precipitate with dilute nitric acid, and no cyanamide was identified (see Ewan, *op. cit.*).

Volumetric Method.—An attempt was made to work out a volumetric method for the estimation of inorganic ferrocyanides based on the formation of the foregoing benzidine hydroferrocyanide. The main difficulty was the discovery of a suitable indicator. After substances of an oxidising nature and salts such as copper sulphate and uranium acetate had proved useless, a suitable reagent was found in a dilute aqueous solution of chlorine or hypochlorite, which gives a distinct yellow coloration with 1 part of benzidine in 100,000 parts of water (compare Ellms and Hauser, *J. Ind. Eng. Chem.*, 1913, **5**, 914).

Free chlorine in solution in water was found to be too volatile when used as an external indicator. The addition of a little sodium carbonate to the dilute solution was sufficient to fix the chlorine. Bromine was found to be even more satisfactory when used in this way.

The indicator is made by adding just sufficient sodium carbonate solution to decolorise 100 c.c. of water containing a few drops of bromine water.

A standard solution of benzidine dihydrochloride is made by dissolving a weighed quantity of the pure salt in water so that the solution is unsaturated at the ordinary temperature (Cumming, *J. Soc. Chem. Ind.*, 1923, **42**, 166). If the benzidine dihydrochloride is not very pure, the quantity in solution may be accurately estimated by means of sodium nitrite.

The solution of the ferrocyanide, which must be neutral, is titrated with the standard neutral benzidine solution. A white precipitate forms immediately. When somewhat less than the approximate volume of benzidine required for complete precipitation (determined by a preliminary trial) has been run in with constant stirring, a drop of the mixture is placed on filter-paper. Here the white precipitate decomposes in the air and a blue centre forms surrounded by a colourless ring of solution. A drop of the bromine indicator placed nearby is allowed to spread and touch the colourless ring; a yellow coloration appearing at the juncture denotes the end-point. Even before titration is completed, a yellow coloration will appear if the bromine touches the blue centre, so that care must be taken that the yellow coloration is

produced in the colourless ring. The tests must be made as quickly as possible.

The method was tested against sodium and potassium ferrocyanides. Fifty c.c. of a standard solution of $K_4Fe(CN)_6,3H_2O$ (2 grams in 500 c.c.) required 61·2, 60·9, 60·9 c.c. of a standard solution of benzidine dihydrochloride (3 grams in 500 c.c.); theo. requires 60·9 c.c. 0·25 Gram and 0·20 gram of $Na_4Fe(CN)_6,10H_2O$ required 67 c.c. and 53·2 c.c., respectively, of the benzidine solution (theo. = 66·35 c.c. and 53·08 c.c.). One gram of $C_{12}H_{12}N_2,2HCl \equiv 0{\cdot}394$ gram of $Na_4Fe(CN)_6$ and 0·477 gram of $K_4Fe(CN)_6$. It is evident that accurate results can be obtained. A satisfactory end-point was not obtained in the reverse process, in which the ferrocyanide solution was run into the benzidine hydrochloride solution.

The same method is applicable to the estimation of an organic base which forms an insoluble hydroferrocyanide in neutral solution.

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XXXIII.—*Chloronitrobenzenes and Thiocarbamides.*

By JOHN TAYLOR and AUGUSTUS EDWARD DIXON.

IN various communications (see, for example, Dixon and Hawthorne, T., 1907, **91**, 122; Dixon and Taylor, T., 1908, **93**, 18), it has been shown that the chlorides of carboxylic acids tend to unite with thiocarbamide and with its non-acylated derivatives, thereby forming salts, apparently of the type $C(NH_2)_2{:}SCl{\cdot}COR$. From these, the elements of hydrogen chloride are easily removable —or may break off spontaneously—the residue being an *iso*thiocarbamide, $NH_2{\cdot}C(:NH){\cdot}S{\cdot}COR$. As a rule, the latter compound is unstable, the acyl group, unless it happens itself to decompose, passing from its engagement with sulphur and becoming linked to one of the nitrogen atoms:

$$NH_2{\cdot}C(:NH){\cdot}S{\cdot}COR \longrightarrow NH_2{\cdot}CS{\cdot}NH{\cdot}COR.$$

There being a certain degree of analogy between the chloronitrobenzenes and the carboxylic acid chlorides, we have sought to learn if the former would play towards thiocarbamide and its derivatives a part similar to that of the acid chlorides mentioned.

Neither *o*- nor *p*-chloronitrobenzene combined with thiocarbamide, nor did 2 : 5-dichloro-1-nitrobenzene. 1-Chloro-2 : 4-dinitrobenzene, however, in the presence of cold acetone, united spon-

taneously with thiocarbamide and with phenylthiocarbamide, the product in each case being a *hydrochloride*, soluble in water, and yielding with picric acid the corresponding *picrate*. From the former, alkali hydroxide withdrew the elements of hydrogen chloride, but without producing either the free *S*-base,

$$NH_2{\cdot}C(:NH){\cdot}S{\cdot}C_6H_3(NO_2)_2,$$

or its *N*-isomeride: instead, the dinitrophenyl residue broke off as dinitrophenyl mercaptan, $(NO_2)_2C_6H_3{\cdot}SH$, a behaviour analogous to that of the alkyl *iso*thiocarbamides (compare Claus, *Ber.*, 1874, **7**, 236; 1875, **8**, 41; Klinger, *Ber.*, 1878, **11**, 492; 1879, **12**, 575; Werner, T., 1890, **57**, 283).

When the components were heated together in alcohol, a yellow, crystalline solid was deposited, consisting mainly of tetranitrodiphenyl disulphide, a substance which, according to Willgerodt (Privatmitth., Beilst., II, 3 ed., 816), is formed when a solution of the above mercaptan is exposed to the air. The essential changes, therefore, are as follows (Dn = the dinitrophenyl group):

$$2NH_2{\cdot}C(:NH){\cdot}S{\cdot}Dn \longrightarrow 2Dn{\cdot}SH \longrightarrow Dn{\cdot}S{\cdot}S{\cdot}Dn.$$

With thiocarbanilide, in boiling alcohol, chlorodinitrobenzene gave at first a little of the nearly pure disulphide; on further boiling, the solution became deep red, with liberation of phenylthiocarbimide, and from the cooled liquor the dinitrodiphenylamine, $(NO_2)_2C_6H_3{\cdot}NHPh$, of Clemm (*Ber.*, 1870, **3**, 128) was deposited.

That the dinitrophenyl radicle should have migrated from sulphur to nitrogen seemed highly improbable; the more so, as no trace of dinitrophenylthiocarbanilide could be isolated. Further experiment showed that thiocarbanilide, when boiled in nearly absolute alcoholic solution, decomposes slowly into aniline and phenylthiocarbimide (most of the latter, combining with the alcohol, yielded phenylthiourethane, m. p. 68—69°). The slow production of dinitrodiphenylamine is therefore attributable to the gradual liberation of aniline, which, as fast as it is formed, reacts with the chlorodinitrobenzene.

In no respect, therefore, is the behaviour of chlorodinitrobenzene towards thiocarbamides that to be expected of an ordinary acyl chloride; moreover, with alkali thiocyanate, it yields, not a thiocarbimide, but a thiocyanate (Austen and Smith, *Amer. Chem. J.*, 1886, **8**, 90), whereas practically all carboxylic acid chlorides yield thiocarbimides.

Picryl chloride, it was anticipated, might yield with thiocarbamide the salt of a base, $NH_2{\cdot}C(:NH){\cdot}SPi$, spontaneously changing into picrylthiocarbamide, $NH_2{\cdot}CS{\cdot}NHPi$. For, according to Crocker (T., 1902, **81**, 436; see also Crocker and Lowe, T., 1904,

85, 646), picryl chloride reacts with ammonium thiocyanate in the presence of certain alcohols, yielding an alkyl picryl picriminothiocarbonate, for example, PiN:C(OEt)·SPi, the occurrence of which is attributed to the initial formation of picrylthiocarbimide, Pi·NCS.

In practice, the foregoing anticipation was not realised. Interaction took place spontaneously, with the formation of an additive compound, or salt, from which the corresponding *picrate* and the *salicylate* were obtained. Neither the base nor its transposition product could be isolated, the picryl group breaking away with the sulphur, partly in the form of picryl sulphide, and partly in the form of a maroon-coloured powder, which was not identified. With phenylthiocarbamide, very little salt resulted, the main product, even in the cold, being picryl sulphide, together with the maroon-coloured solid. Thiocarbanilide behaved similarly, except that it gave no salt at all.

That the migration of the acyl group, R, in a base NH_2·C(:NH)·SR to the unsaturated nitrogen atom is not due solely to the electronegative character of the radicle, the foregoing results make abundantly clear. Whether the radicle moves, or no, depends evidently on the " pull " of the unsaturated nitrogen, against the hold of the sulphur atom; a hold, doubtless influenced by the number and nature of other substituents in the thiocarbamidic fraction of the molecule. The tenacity with which the nitrophenyl residues cling to sulphur is in sharp contrast with the comparative reluctance of that element to remain conjoined with the group R·CO· when the latter is markedly electronegative. This group, as a rule, is by no means reluctant towards combination with tervalent nitrogen.

In general, the disruption of the additive compounds of thiocarbamide and its derivatives with the chloronitrobenzenes is precisely similar to that of its combinations with alkyl salts. The mercaptoid bases of the latter, if procurable at all, are mostly unstable, decomposing spontaneously, with the formation of a mercaptan or of a disulphide. Those of the nitrophenyl chlorides, so far obtained, even as salts, are still more unstable.

Having regard to the observations now made with picryl chloride and thiocarbamides, we find some difficulty in reconciling them with the explanation given by Crocker and Lowe (*v. supra*). Using as solvent an alcohol which failed to yield a picriminothiocarbonate (presumably because it could not unite with the supposed picrylthiocarbimide to form a thiourethane), and removing from the interaction product a relatively large amount of picryl sulphide, they isolated a compound which gave the analytical figures required

for trinitrophenylthiocarbimide. To the compound, however, they assign the formula Pi·SCN and the name "picryl thiocyanate." It is conceivable, of course, that picrylthiocarbimide, directly formed from picryl chloride and ammonium thiocyanate, unless it finds something to unite with, may undergo transformation into the isomeric thiocyanate. Unfortunately, the authors have given no reason for supposing the so-called "picryl thiocyanate" to be a thiocyanate; nor do they seem to have inquired whether the product, when treated with alcohol and picryl chloride, affords ethyl picryl picriminothiocarbonate.

Except as a side-issue, we have no concern with this very remarkable reaction. It does not occur with chlorodinitrobenzene and ammonium thiocyanate in boiling absolute alcohol, the product being the dinitrophenyl thiocyanate of Austen and Smith (*loc. cit.*), a trifle impure. With picryl chloride, Crocker's reaction occurs in the cold: in a hot alcoholic solution, it is not obstructed, even by the presence of at least four molecules of ammonium thiocyanate per one molecule of picryl chloride—an excess which one might have anticipated would leave not much picryl chloride available to attack the supposed picrylthiourethane.

Experimental.

Thiocarbamide, in alcoholic solution, was boiled for some days, under reflux, with *o*- and with *p*-chloronitrobenzene, and with 2 : 5-dichloro-1-nitrobenzene. No sign of interaction was observed; the product in each case, when treated with water, gave up to it unchanged thiocarbamide, the solution remaining clear on the addition of picric acid.

1-*Chloro*-2 : 4-*dinitrobenzene and Thiocarbamide.*—Molecular proportions of the components were heated under reflux in alcoholic solution, small yellow needles being gradually deposited, which proved to consist of slightly impure tetranitrodiphenyl disulphide. With hot glacial acetic acid, a like result was obtained, and with boiling acetone; in the last case, however, the filtered liquor, on cooling, gave a crystalline magma, partly soluble in water, the solution (which contained free thiocarbamide) yielding a sparingly soluble *picrate*.

A solution of the components in cold acetone, when kept for several days in a closed vessel, deposited a pad of exceedingly fine, woolly needles, from which the entangled liquor could not entirely be separated. The dry substance melted at about 152—153°, with darkening and effervescence; when heated over a small flame, it exploded. In cold water, it dissolved, yielding an acid, slightly opalescent solution, becoming turbid on heating; with

sulphuric acid, it effervesced, giving off hydrogen chloride [Found : HCl (by direct titration) = 13·03; S = 10·85. $C_7H_7O_4N_4ClS$ requires HCl = 13·10; S = 11·49 per cent.].

The *picrate*, identical with the foregoing picrate, crystallised from water in fine, yellow needles, melting with decomposition and effervescence at 192—193° (uncorr.) : when heated over a small flame, it exploded, leaving a voluminous mass of carbon (Found : S = 6·85. $C_{13}H_9O_{11}N_7S$ requires S = 6·79 per cent.).

With warm alkali hydroxide, the hydrochloride gave a deep bromine-red solution, bleached by acid, with the precipitation of a yellow solid, having the properties of dinitrophenyl mercaptan. The alkaline mixture, when boiled with a salt of lead, yielded no trace of lead sulphide, and hence contained no dinitrophenylthiocarbamide.

1-*Chloro*-2 : 4-*dinitrobenzene and Phenylthiocarbamide.*—In general, when heat was used, the results were similar to the preceding, and need not be described in detail. From a solution of the components in cold acetone, pale yellow, feathery prisms were slowly deposited, melting with decomposition at 98—100°, and showing the properties of a hydrochloride. The substance, which gave rather poor figures for HCl and for S, was recrystallised from chloroform, its m. p. now being sharp at 100° (Found : S = 9·22. $C_{13}H_{11}O_4N_4ClS$ requires S = 9·02 per cent.). Its aqueous solution —which became turbid on standing—yielded with silver nitrate a yellow precipitate, partly soluble in nitric acid (silver cyanamide); the mixture became orange with ammonia, but was not blackened by boiling. With alkali hydroxide, it gave a deep bromine-coloured solution, from which, on boiling with a salt of lead, no trace of lead sulphide was precipitated. Like the preceding hydrochloride, it gave with aqueous picric acid a bright yellow *picrate*, nearly insoluble in cold water; m. p. 160—161° with effervescence.

1-*Chloro*-2 : 4-*dinitrobenzene and Thiocarbanilide.*—The materials, when heated in alcohol under reflux, behaved as usual, a crystalline solid being deposited in small amount, consisting of nearly pure tetranitrodiphenyl disulphide (Found : S = 15·52. Calc., S = 16·1 per cent.). On prolonged boiling of the filtrate, the odour of phenylthiocarbimide became strongly marked, and when the now deep red liquor was filtered from a further trace of the disulphide and let cool, brilliant, crimson needles separated, in appearance rather like chromic anhydride : they were free from chlorine and sulphur, and consisted of nearly pure dinitrodiphenylamine, $(NO_2)_2C_6H_3{\cdot}NH{\cdot}C_6H_5$. After recrystallisation from alcohol, they were identified by comparison with a pure specimen of that compound, and by the mixed melting point, 156—157°.

From a solution of the components (9 grams) in cold acetone, yellow prisms were slowly deposited, the amount at the end of a fortnight being a little more than 0·5 gram. They were free from chlorine, did not melt at 220°, exploded when fused on a spatula, and were not desulphurised by boiling with a hot, alkaline solution of lead acetate. The conjecture that this might possibly be the *iso*-base, NHPh·C(:NPh)·SDn, requiring S = 8·12 per cent., was negatived by analysis (Found : S = 15·1 per cent.). Apparently, it was the usual tetranitrodiphenyl disulphide (S required = 16·1 per cent.).*

Picryl Chloride and Thiocarbamide.—These substances interact very readily. When picryl chloride (1 mol.) was added to a suspension of finely powdered thiocarbamide in cold acetone, the mixture forthwith became clear, and when poured into water gave no turbidity; hence the whole of the picryl chloride had entered into combination. The aqueous mixture, when treated with a solution of picric acid, gave a bright yellow picrate, m. p. 149—150°; this contained S = 6·20 per cent., and therefore was the expected *picrate* of picryl-*S*-thiocarbamide, $C(NH_2)_2{:}SPi{\cdot}OPi$ ($C_{13}H_8O_{13}N_8S$ requires S = 6·20 per cent.). Further, with sodium salicylate, it gave a precipitate of the corresponding *salicylate*, m. p. 76° (Found : S = 7·35. $C_{14}H_{11}O_9N_5S$ requires S = 7·53 per cent.).

Neither substance was desulphurised by boiling with the alkaline solution of a salt of lead; the original solution, when thus treated, gave a derivative of picryl mercaptan.

Thiocarbamide-picryl chloride is very unstable. When the solution in acetone was allowed to evaporate, a red, sticky oil was left, which presently hardened to a mixture, partly yellow and partly maroon-coloured. Water dissolved the yellow component, the solution affording with picric acid the above picrate; the

* The analytical figure for S in this compound is often deficient. Willgerodt (*Ber.*, 1877, **10**, 1686), who at the time thought it to be dinitrophenyl mercaptan, obtained—except in the case of one carbon determination—satisfactory numbers for C, H, and N, but had to rest content with S = 13·7. In numerous analyses of this substance (made by evaporation to dryness in a silver crucible with pure sodium hydroxide, and fusion of the residue with nitre), our highest figure was 15·52 per cent. Mostly, it was round about 15; but we have got as low as 13·9, from a material apparently well purified. In no case was a sulphuretted odour perceived during the evaporation.

Curiously, Willgerodt obtained the disulphide from chlorodinitrobenzene and thiocarbamide : it was not until the experimental work of this paper had been finished that we happened on his communication. In the private note to "Beilstein," already mentioned, he refers to the real dinitrophenyl mercaptan as melting at 131° : this was confirmed by Hinsberg (*Ber.*, 1907, **39**, 4331).

remainder dissolved readily in alcohol. From the deep-red solution, however, yellow crystals were soon deposited; when recrystallised from glacial acetic acid, they formed brilliant yellow spangles of dipicryl sulphide, m. p. 226—227° (Found: S = 6·77. Calc., S = 7·02 per cent.). Later, a maroon-coloured powder separated, melting indefinitely, but completely liquefied at 226—227°: in different preparations, the sulphur varied between 6·8 and 8·4 per cent., and the material was not identified. Probably it originates through the reduction of one or more nitro-groups in the picryl radicle or radicles of dipicryl sulphide. At all events, picric acid, and picryl chloride, when brought into contact with sodium cyanamide, potassium cyanide, and other reducing agents, were found to yield materials having a deep maroon colour, similar to that of the foregoing powder.

From thiocarbamide and picryl chloride, in the presence of hot alcohol, little or no picryl-*S*-thiocarbamide salt was formed, the only products isolated being dipicryl sulphide and the maroon-coloured powder.

Picryl Chloride and Phenylthiocarbamide.—A mixture of the two, when heated on the water-bath, exploded.

A suspension of phenylthiocarbamide in cold acetone, when treated with picryl chloride, became clear, developing a deep red coloration. On the addition of water, a red oil was precipitated, the filtrate from which gave only a trifling amount of picrate.

When glacial acetic acid was substituted for the acetone, the phenomena were similar, but the aqueous portion yielded a more copious precipitate with picric acid. The product was difficult to purify, and the highest melting point observed was 82°; nevertheless, it consisted essentially of picryl-*S*-phenylthiocarbamide picrate (Found: S = 5·56. Calc., S = 5·40 per cent.).

When kneaded with water, the oil changed to a solid, most of which dissolved readily in alcohol; the remainder was identified as dipicryl sulphide. From the alcoholic solution, a deep maroon-coloured powder was deposited, not containing the above sulphide. It was free from halogen, decomposed between 120 and 122°, and yielded on analysis 6·17 per cent. of sulphur.

Picryl Chloride and Thiocarbanilide.—From these, although they interact readily, no trace of additive salt could be obtained. Otherwise, the result was similar to that in the preceding case, dipicryl sulphide being isolated, together with the maroon-coloured powder. The components were boiled together in alcohol but, in the deep red product, no trace could be found of picrylanilide, Pi·NHPh, nor was phenylthiocarbimide liberated.

In conclusion, we desire to thank the United Alkali Company, who kindly presented us with liberal specimens of *o*- and *p*-chloronitrobenzene, dichloronitrobenzene, and chlorodinitrobenzene.

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XXXIV.—*Intermittent Current Electrolysis. Part III. The Measurement of Overvoltage.**

By SAMUEL GLASSTONE.

IT has been shown in a previous paper (T., 1923, **123**, 2926) that the back *E.M.F.* of a polarised lead electrode measured by the commutator method varies to some extent with the arrangement of the apparatus. When the polarised electrode always forms part of a complete circuit, and this circuit contains self- and mutual-inductance, the potential registered when the polarising current is off is often higher than that obtained in the ordinary commutator method, in which there is no complete circuit when the polarising current is switched off (see Part II, *loc. cit.*, p. 2928, methods IIc and I*a*, respectively). An examination of the figures quoted in the previous paper shows, however, that although differing potentials are obtained when the polarising current is off, yet when the current is on, the potential of the electrode appears to be almost independent of the arrangement of the apparatus. It seems, therefore, that the

* The term "overvoltage" (Überspannung) appears to have been first used by Caspari (*Z. physikal. Chem.*, 1899, **30**, 89) to denote the excess potential over the thermodynamically reversible value which has to be applied to an electrode before visible gas evolution can *commence*. Tafel (*ibid.*, 1905, **50**, 641) has extended the use of the term by considering overvoltage as the difference in potential between an electrode at which gas is being evolved by electrolysis at a *definite current density*, and a reversible gas electrode in the same electrolyte. Clearly this difference in potential should be measured while gas is being evolved, that is, while the polarising current is flowing, but in these circumstances, in the usual method of measurement, the presence of a resistance at the surface of the test electrode causes an error in the measured potential. This error must be eliminated, and the true overvoltage, which is considered in the present paper, refers to the difference between the potential of the reversible electrode and that of the polarised electrode *while the current is on*, measured by some device which eliminates any error due to resistance. It is shown later that the potential of the electrode while current is flowing is probably identical with the back *E.M.F.* obtained *immediately* the current is switched off, hence if the so-called "polarisation overvoltage," measured by the back *E.M.F.* of the electrode, were only determined in a proper manner it would be found to be the same as the true overvoltage.

true overvoltage of the electrode is always the same, but at the instant of switching off the current some change takes place which depends, amongst other things, on the induction of the circuit. With a view to investigate this point further, the rate of fall of the potential of various electrodes, after cutting off the polarising current, was measured with the two different arrangements I*a* and II*c* by means of the rotary commutator described in the previous paper. The commutator was set so as to measure the potential of an electrode at average times of 0·002, 0·004, 0·006, and 0·012 second after the polarising circuit was broken; in each case the electrode was connected to the potentiometer system only for an extremely short period at a time, hence the potentials measured may be regarded as instantaneous potentials. The results obtained were plotted on a *P.D.*–time graph, and the curve was extrapolated to zero time. The value so obtained is probably the true potential of the electrode at the instant at which the polarising current was switched off, and from it the overvoltage of the electrode may be calculated. The results obtained indicate that in general the rate of fall of potential in method I*a* is greater than in method II*c*, consequently the potentials measured at some short time after the polarising current is cut off will be lower in the former case. On extrapolating to zero time, however, it has been found that both methods give, as is only to be expected, as nearly as possible identical potentials. The varying rate of fall may be attributed to the fact that in method II*c* a very small current still flows in the circuit even when the polarising current is off, and also to the possibility that the sudden discharge of current at the instant of switching off, which probably occurs in method I*a*, may cause a more rapid removal of the electromotively active material which has accumulated at the electrode.

Many of the figures quoted in the literature which purport to give the influence of alternating current on the potential of an electrode polarised by direct current are erroneous, since they are based, as has been already pointed out (see Part II), on a false assumption; unpublished experiments by the present author have shown, however, that even small alternating currents are able to reduce the hydrogen overvoltage at lead, platinum, tin, and silver electrodes. The action of the alternating current is probably to increase the speed of the " compensating processes " which prevent the accumulation of the electromotively active material at the electrode; it is therefore possible that a sudden rush of induced current will have a similar effect and cause the potentials of certain electrodes to decrease at a rate which is greater than the normal rate of fall.

With lead electrodes of 1 sq. cm. exposed area, it has been found

that the overvoltages measured by the extrapolation method described above are almost identical with those obtained by the direct method at current densities up to 0·012 amp. per sq. cm.; it is therefore doubtful whether the large "transfer resistance" (compare Newbery, *Trans. Faraday Soc.*, 1919, **15**, 126) has any real existence. At higher current densities the two sets of values diverge, and at 0·24 amp. per sq. cm. there is often a difference of 0·10 to 0·20 volt, corresponding to a resistance of 0·5 to 1·0 ohm. This resistance is probably due to the metal–gas–electrolyte system situated at the surface of the electrode (Part II, *loc. cit.*), and experiments in which electrodes of various sizes were used with dilute solutions at various temperatures have yielded results which lend considerable support to this view.

The results obtained in this work throw some light on the observations made by some authors, for example, Newbery (T., 1922, **121**, 7) and Sand, Weeks, and Worrell (T., 1923, **123**, 456), which indicate that the potentials measured by the ordinary commutator method approach a constant value as the speed of the commutator is increased towards 2,000 to 3,000 revolutions per minute, yet the values so obtained are much below the potentials measured by the direct method. In the method which appears to have been used by the authors mentioned above, the potential measured is the average potential over almost the whole of the period in which the current is off; during the whole of this time, however, the potential is falling and the fall for a small lead cathode in sulphuric acid may even amount to as much as 0·2 volt in 0·01 sec., which is the period of contact with the potentiometer circuit for a commutator speed of 3,000 revs. per minute. From the *P.D.*–time curves obtained after switching off the polarising current it has been possible to estimate the average potentials during certain periods corresponding to the times of contact with the potentiometer system for various commutator speeds; the curves are of the form found for a mercury cathode in sulphuric acid by Newbery (*loc. cit.*), giving an apparently constant value at high speeds, which is, however, often from 0·10 to 0·14 volt below the true potential as measured by the extrapolation method described in this paper.

It has been suggested previously (T., 1923, **123**, 1745) that direct and commutator potentials may not be comparable at the same apparent current densities, since in the latter case the electromotively active material is being removed from the electrode during the whole of a cycle, but is only being regenerated during half of a cycle. At fairly high current densities the electrode reaches its equilibrium potential very rapidly and the fact that the current has been off for half of the time makes very little difference; at

low current densities, however, for example, below 0·001 amp. per sq. cm., the maximum potential reached while the current is flowing when the commutator is working, is much below that obtained by the direct method for the same current density. As the temperature is raised, this effect becomes noticeable at much higher current densities. Hence commutator overvoltages are not comparable with those obtained by the direct method at very low current densities.

The experiments described in this paper were carried out with lead electrodes, but further experiments on similar lines with mercury, copper, iron, nickel, and nickel–iron alloy electrodes have so far given very similar results. It is hoped to publish an account of these later.

Experimental.

Apparatus.—The apparatus used was the same as described in a previous paper (Part II), the arrangements I*a* and II*c* only being used. The rheostat of the motor driving the commutator was calibrated to give speeds of 3,600 and 1,800 changes per minute, and two positions were marked on the commutator to give the potentials at 0·002 sec. and 0·006 sec. for the first speed, and at 0·004 sec. and 0·012 sec. for the second speed, after the polarising current was broken. In this way the necessary alterations to the commutator could be made very rapidly, so that the potentials measured were comparable with one another. The contact maker *c* (Part II, *loc. cit.*, Fig. 1) of the commutator was so adjusted that the electrode was connected to the potentiometer system only for about 0·002 sec. at a time; during this period the fall of potential is comparatively small, hence the results obtained may be regarded as instantaneous values of the potential.

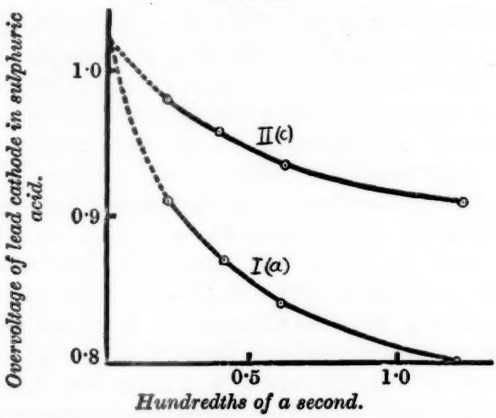
Method of Experiment.—In the first set of experiments a lead electrode of 1 sq. cm. exposed area was used; it was in every case previously polarised for some time until its potential was practically constant. By suitable adjustment of the commutator the potential of the electrode at the end of the period in which the current was on was measured by the direct method, and then the back *E.M.F.'s* were determined, as described above, at various times after the polarising current was switched off. These experiments were repeated at a number of different current densities for the two arrangements of apparatus I*a* and II*c*. The measurements by the direct method were then repeated without the use of the commutator in order to ascertain whether the electrode had had sufficient time to reach its equilibrium potential before the current was switched off when the commutator was being used. As mentioned above,

failure to attain equilibrium was found to occur only at very low current densities, and these cases are marked with an asterisk in the tables of results.

In a new set of experiments all the measurements were repeated under as nearly as possible identical conditions with an electrode of 7·5 sq. cm. exposed area; a comparison of the results obtained with the large and small electrodes has proved interesting.

Results.—In Table I there is given a typical set of results obtained at room temperature (15°) for the rate of fall in potential of an electrode after the polarising current had been switched off. The electrodes were of the smaller type (1 sq. cm. area); A refers to a lead anode in *N*-sodium hydroxide; B to a cathode in the same electrolyte; C to an anode, and D to a cathode in *N*-sulphuric acid.

FIG. 1.



Figures for the two arrangements of apparatus are given. The values marked "Extrapolated" are those obtained for zero time by the extrapolation method from the *P.D.*–time curves, only one pair of which is shown in Fig. 1 to economise space.

TABLE I.

Time after switching off current (sec.).	A.		B.		C.		D.	
	I (*a*).	II (*c*).	I (*a*).	II (*c*).	I (*a*).	II (*c*).	I (*a*).	II (*c*).
0·002	0·93	0·96	1·015	1·03	1·00	1·00	0·91	0·98
0·004	0·90	0·94	0·97	1·00	0·99	0·99	0·87	0·955
0·006	0·875	0·925	0·93	0·97	0·985	0·985	0·84	0·935
0·012	0·84	0·89	0·85	0·90	0·98	0·98	0·80	0·91
Extrapolated	0·99		1·07		1·015		1·02	

With the larger electrode, it was almost invariably found that the rate of fall was not so great as with the small electrode, but the general behaviour was the same.

TABLE II.

Small electrodes (1 *sq. cm.*).

Electrode A.							
C.D. (amp./cm.^{2}) ...	0·006	0·012	0·018	0·030	0·060	0·12	0·24
Direct (volts)	0·99	1·03	1·07	1·13	1·18	1·24	1·30
Extrapolated	0·98	1·01	1·03	1·04	1·06	1·08	1·09
Difference	0·01	0·02	0·04	0·09	0·12	0·16	0·21
Electrode B.							
C.D.	0·006	0·012	0·018	0·030	0·060	0·12	0·24
Direct	0·80	0·94	1·04	1·14	1·22	1·28	1·35
Extrapolated	0·79	0·91	1·00	1·06	1·09	1·11	1·13
Difference	0·01	0·03	0·04	0·08	0·13	0·17	0·22
Electrode C.							
C.D.	0·006	0·012	0·018	0·030	0·060	0·12	0·24
Direct	0·98	1·02	1·05	1·08	1·12	1·18	1·25
Extrapolated	0·97	1·00	1·03	1·06	1·08	1·09	1·11
Difference	0·01	0·02	0·02	0·02	0·04	0·09	0·14
Electrode D.							
C.D.	0·006	0·012	0·018	0·030	0·060	0·12	0·24
Direct	0·83	0·87	0·92	0·95	0·96	0·97	1·02
Extrapolated	0·82	0·83	0·83	0·84	0·85	0·86	0·86
Difference	0·01	0·04	0·09	0·11	0·11	0·11	0·16

Large electrodes (7·5 *sq. cm.*).

Electrode A.							
C.D.	0·0008	0·0016	0·0024	0·004	0·008	0·016	0·032
Direct	0·58*	0·87	0·91	0·97	1·03	1·10	1·17
Extrapolated	0·57*	0·86	0·90	0·94	0·97	1·00	1·03
Difference	0·01	0·01	0·01	0·03	0·06	0·10	0·14
Electrode B.							
C.D.	0·0008	0·0016	0·0024	0·004	0·008	0·016	0·032
Direct	0·50*	0·75	0·84	0·94	1·05	1·17	1·30
Extrapolated	0·49*	0·73	0·77	0·84	0·90	0·96	1·04
Difference	0·01	0·02	0·07	0·10	0·15	0·21	0·26
Electrode C.							
C.D.	0·0008	0·0016	0·0024	0·004	0·008	0·016	0·032
Direct	0·84	0·91	0·96	1·02	1·08	1·14	1·22
Extrapolated	0·83	0·85	0·89	0·93	0·99	1·03	1·07
Difference	0·01	0·06	0·07	0·09	0·09	0·11	0·15
Electrode D.							
C.D.	0·0008	0·0016	0·0024	0·004	0·008	0·016	0·032
Direct	0·60*	0·76*	0·82	0·88	0·94	0·99	1·04
Extrapolated	0·57*	0·71*	0·77	0·79	0·81	0·84	0·85
Difference	0·03	0·05	0·05	0·09	0·13	0·15	0·19

* Equilibrium not reached; see p. 254.

In Table II are given the overvoltages as measured by the direct method at the end of the period during which the polarising current was on (marked "direct") and also the extrapolated values obtained as described above, which are believed to be the true overvoltages at the various current densities. (It should be noted that the current densities given in this paper are obtained from the actual value of the current in the circuit and not the average values

as indicated on an ammeter. Previous workers with the commutator do not appear to have made this point clear.)*

In Table III there are brought together for the sake of comparison some overvoltage values for the same current densities obtained with the two electrodes by the different methods of measurement.

TABLE III.

	Electrode A.				Electrode B.			
	Direct.		Extrapolated.		Direct.		Extrapolated.	
C.D.	Large.	Small.	Large.	Small.	Large.	Small.	Large.	Small.
0·008	1·03	1·00	0·97	0·99	1·05	0·85	0·90	0·84
0·016	1·10	1·06	1·00	1·02	1·17	1·02	0·96	0·97
0·032	1·17	1·13	1·03	1·04	1·30	1·15	1·04	1·06
	Electrode C.				Electrode D.			
0·008	1·08	0·99	0·99	0·98	0·94	0·85	0·81	0·82
0·016	1·14	1·04	1·03	1·02	0·99	0·90	0·84	0·83
0·032	1·22	1·08	1·07	1·06	1·04	0·95	0·85	0·84

Discussion of Results.

The results given above show that for small values of the polarising current the overvoltages measured by the direct method and by the extrapolation method are almost the same, hence the existence of a "transfer resistance," which is supposed to be very great at low current densities (compare Newbery, *Trans. Faraday Soc.*, 1919, **15**, 126), is very doubtful. The potentials measured by McInnes and Adler (*J. Amer. Chem. Soc.*, 1920, **42**, 194) at very low current densities therefore appear to be true overvoltages and not due, as Newbery suggests (*ibid.*, 1920, **42**, 2007), to transfer resistance only. For current values below about 0·01 amp., almost independent of the size of the electrode, it appears that the direct method is the most convenient method for the measurement of overvoltage; in fact for very low current densities it is the only method available, since the repeated make and break of the polarising current circuit prevents the electrode from ever reaching its equilibrium value. At greater current densities, however, the results obtained by the direct method are appreciably higher than the extrapolated values, and this difference is believed to be due to the resistance of the metal–gas–electrolyte system at the surface of the electrode; this resistance appears to be not greater than 4 ohms per sq. cm. of the electrode surface, and is often much less.

The figures brought together in Table III show clearly that for fairly large values of the polarising current the potentials measured by the direct method depend on the size of the electrode,

* See, however, Sand and Weeks (T., 1923, **123**, 2896), which appeared after the completion of this work.

but those obtained by the extrapolation method are almost independent of the area of the electrode. To show that these differences were not due to differences in the state of the surface of the two electrodes, a portion of the large electrode was waxed over, leaving only 1 sq. cm. exposed, and the experiments were repeated; the results obtained were almost identical with those obtained with the small electrode. The fact that the extrapolation method yields results that appear to be independent of the electrode size does not of course prove these to be the true overvoltages, but since the potentials obtained by the direct method may be varied at will by altering the size of the exposed portion of the electrode, the former results are more worthy of consideration. According to the results given above (Table III), it is to be expected that, with an electrode of very small area, the potentials measured by the direct method will approach very closely those obtained by the extrapolation method; in these circumstances, however, the current densities are very uncertain, since much of the surface is covered with bubbles.

Temperature Experiments.

In order to obtain further experimental evidence on the question of "surface resistance," the overvoltages of the various electrodes were determined by the direct and extrapolation methods at three different temperatures, namely 10°, 40°, and 70°. Since the resistance of an electrolyte decreases with increasing temperature, whilst at the same time the rate of diffusion into the surface layer is increased, it was thought possible that the "surface resistance" might decrease with increasing temperature. On the other hand, if the difference between the direct and extrapolation potentials at high current densities was due to an extremely rapid initial fall of potential which had not been allowed for in the extrapolation method, it was considered probable that the error would be increased at higher temperatures.

Some difficulty was experienced in finding a suitable substance with which to insulate completely all except the face of the test electrode, and which would remain intact at a temperature of 70°; eventually ordinary "rubber solution" was used, but even this was not quite satisfactory, and so all the results contained some error due to the fact that not all the current lines ended on the plane surface of the electrode with which the jet of the connecting tube of the standard electrode was in contact. As the temperature increased, it was found that at the lower current densities the electrodes did not reach their equilibrium potentials when the commutator was working, so only the results obtained with the large

electrodes (7·5 sq. cm. area) for the higher current values are given in Table IV.

TABLE IV.

Electrode A.	10°.			40°.			70°.		
C.D.	Direct.	Extrap.	Diff.	Direct.	Extrap.	Diff.	Direct.	Extrap.	Diff.
0·004	1·06	0·95	0·11	0·85	0·77	0·08	0·65	0·59	0·06
0·008	1·17	1·02	0·15	0·95	0·83	0·12	0·79	0·67	0·12
0·016	1·26	1·06	0·20	1·06	0·89	0·17	0·88	0·72	0·16
0·032	1·34	1·09	0·25	1·16	0·94	0·22	0·98	0·78	0·20
Electrode B.									
0·008	1·13	0·90	0·23	1·01	0·80	0·21	0·91	0·71	0·20
0·016	1·24	0·96	0·28	1·12	0·86	0·26	1·00	0·76	0·24
0·032	1·33	1·00	0·33	1·22	0·91	0·31	1·08	0·81	0·27
Electrode C.									
0·004	1·06	0·94	0·12	0·99	0·87	0·12	0·87	0·79	0·08
0·008	1·12	0·98	0·14	1·04	0·92	0·12	0·92	0·83	0·09
0·016	1·18	1·00	0·18	1·09	0·94	0·15	0·98	0·86	0·12
0·032	1·23	1·05	0·18	1·14	0·97	0·17	1·04	0·88	0·16
Electrode D.									
0·004	0·98	0·80	0·18	0·94	0·78	0·16	0·88	0·75	0·13
0·008	1·02	0·81	0·21	0·97	0·79	0·18	0·91	0·77	0·14
0·016	1·06	0·82	0·24	1·00	0·80	0·20	0·95	0·78	0·17
0·032	1·10	0·83	0·27	1·04	0·81	0·23	0·99	0·79	0·20

These results show that there is a distinct tendency for the difference between the direct and the extrapolation method to decrease as the temperature increases; as indicated above, this may be taken as evidence in favour of the inclusion in the surface resistance of the resistance of a film of electrolyte close up to the surface of the electrode.

Influence of the Concentration of Electrolyte.

It was anticipated that the alteration of the concentration of the electrolyte would influence the potential measured by the direct method to a greater extent than that obtained by the extrapolation method. Experiments were therefore carried out in which the electrolytes were either more dilute or more concentrated than those hitherto used. When using 6*N*-sulphuric acid or 6*N*-sodium hydroxide, the differences between the two sets of overvoltage values were greatly decreased at the higher current densities. When the electrolyte was only of *N*/16 concentration, the surface resistance increased, especially in the case of a lead anode in sodium hydroxide and of a lead cathode in sulphuric acid; at higher temperatures the differences were appreciably diminished. If these dilute solutions were saturated with sodium sulphate, the error due to surface resistance was found to decrease greatly. The evidence on the whole is definitely in favour of the existence of a thin film of electrolyte at the surface of the electrode which will influence the

potential measured by the direct method. A fuller account of the experimental work and a discussion of it must be left for a subsequent communication.

Overvoltage and Current Density.

Tafel (*Z. physikal. Chem.*, 1905, **50**, 668) deduced theoretically that the connexion between overvoltage and current density should be given by an equation of the form $E = a + b \log C$, where E is the overvoltage at the current density C, and a and b are constants. Measurements made by the direct method appear to agree fairly well with this formula (Tafel, *loc. cit.*; Lewis and Jackson, *ibid.*, 1906, **56**, 193; Zerbes, *Z. Elecktrochem.*, 1912, **18**, 627), whereas those made by the ordinary commutator method (Newbery, T., 1916, **109**, 1051, 1066) vary very little with the current density, and in fact often decrease as the current increases. When the overvoltages obtained in the present work were plotted on a graph against log C, the points were found to lie roughly on a straight line in every case, and the following values were obtained for a and b when the current density was expressed in milliamps. per sq. cm.

TABLE V.

	a.	*b*.
Electrode A.	0·84	0·117
„ B.	0·73	0·18
„ C.	0·87	0·11
„ D.	0·76	0·050

The overvoltages calculated from these values were in close agreement with the observed overvoltages, the difference between the two values was never more than about 0·05 volt, and as a rule much less.

Comparison of Old and New Commutator Methods.

It has been already pointed out (p. 251) that the older commutator method gives the average potential over a comparatively long period during the whole of which the potential of the electrode falls more or less rapidly. In the present work, no measurements have been made by this method, but by means of the curves which give the fall in potential after the polarising current is switched off it is possible to determine the average potential of an electrode, during certain periods, corresponding to definite commutator speeds. The overvoltage values so obtained are given in Table VI, together with the extrapolation overvoltages for purposes of comparison.

These figures show that as the commutator speed is increased the back *E.M.F.* increases, at first fairly rapidly and then much more slowly, leading to the impression that a constant value is being rapidly

TABLE VI.

Commutator speed (revs. per min.).	Electrode A.	Electrode B.	Electrode C.	Electrode D.
3600	0·90	0·97	0·995	0·88
3300	0·90	0·965	0·99	0·875
3000	0·895	0·955	0·99	0·87
2400	0·885	0·935	0·99	0·855
1800	0·87	0·91	0·99	0·83
1200	0·85	0·865	0·985	0·805
Extrapolated to zero time	0·99	1·07	1·015	1·02

approached *; these apparently constant values have hitherto been considered as the commutator overvoltages, but they may be as much as 0·15 volt, in some cases, below the value obtained by extrapolating the *P.D.*–time curve to zero time.

Conclusion.

By measuring the rate of fall of the potential of a polarised electrode after the polarising current has been switched off and extrapolating on a *P.D.*–time curve, it has been found possible to determine the true potential of the electrode at the instant of switching off the current; from these potentials, obtained at various current densities, the overvoltage at the electrode has been determined. At low current values, the results so obtained are almost identical with those obtained by the direct method, but with larger currents the values diverge. The difference is probably due to the resistance of a metal–gas–electrolyte system situated at the surface of the electrode; experiments in which the size of the electrode and the dilution and temperature of the electrolyte were varied lend strong support to this view. The " surface resistance " at a lead electrode of 1 sq. cm. area in *N*-sodium hydroxide or *N*-sulphuric acid is not more than 4 ohms. The results obtained in this work render doubtful the existence of a " transfer resistance " which is very great at low current densities.

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XXXV.—*Transference Numbers and Ionic Complexity of Hydrofluoric Acid Solutions.*

By CECIL WHITFIELD DAVIES and LAWSON JOHN HUDLESTON.

THE ionic complexity of aqueous solutions of hydrofluoric acid is most directly determined by measurements of the transference number over a wide range of concentration, the results being com-

* The reason for this is discussed elsewhere.

bined with conductivity data. Since, for the latter, we are employing the results of other investigators, we shall postpone the theoretical discussion and calculation to the second part of the paper and give in the first the experimental procedure and the results of the transference measurements.

Part 1. *Experimental.*

The hydrofluoric acid employed was obtained by heating pure potassium hydrogen fluoride in a platinum distilling flask. The side tube was water-jacketed for the greater part of its length, but as this did not suffice for the condensation of the hydrogen fluoride the end was sealed into a wax vessel packed with ice made from pure distilled water. The hot vapours impinged directly on the ice and the resulting solution was allowed to flow out at the bottom into wax vessels for storage. The acid obtained, of strength about 6*N*, was diluted as required with distilled water which had been boiled and cooled out of contact with air to remove all the carbon dioxide. The solution gave no residue when evaporated to dryness in a platinum dish and gave a perfectly sharp end-point when titrated with pure sodium hydroxide solution with phenolphthalein as indicator, which proved it free from silica (see Hudleston and Bassett, T., 1921, **119**, 403).

Alkaline solutions dissolve appreciable quantities of silica from glass containing-vessels and, as this would make the end-point of titrations difficult to determine, special precautions had to be taken in the preparation and storage of the sodium hydroxide solutions. A platinum dish, containing freshly cut pieces of sodium, was placed over water in a water-bath and covered with a bell-jar, the bottom of which was covered by the water. Hydrogen was introduced below the level of the water and escaped by a tube bent so as to prevent any drops of moisture falling back on to the metal. The vigour of the reaction between the water vapour and the sodium could be exactly controlled by the temperature of the water in the bath. When a clear solution was obtained in the dish, it was decanted into vessels of pure paraffin wax and suitably diluted with distilled water purified from carbon dioxide as above. This was standardised against carefully purified succinic acid.

Titrations were carried out in the following manner. Stoppered wax vessels, containing a little phenolphthalein, were weighed, the acid solution added, and the flasks weighed again, then sodium hydroxide was run in direct from the wax container until the red colour appeared, and the whole weighed once more. The slight excess of alkali was then back-titrated with a very dilute standard acid. Thus our concentrations are given in terms of weight

normality, but from the density determinations of Winteler (*Z. angew. Chem.*, 1902, **15**, 33) conversion into figures for volume concentration makes a negligible difference in the transference numbers.

The actual transference cell had also to be made of pure paraffin wax. The final form adopted consisted of two wax U-tubes of uniform cross section, standing side by side in an outer wax vessel, which they nearly filled. The arms were of unequal length, the longer, of about the same height as the outer vessel, closed at the top except for a small hole, bore the electrodes, short pieces of platinum wire, the shorter were open at the top and stood about 2 cm. below the level of the liquid in the outer vessel. In use, therefore, the gases were generated near the surface of the liquid in the longer arms, thus causing but little stirring, escaped into the gas space above within the tube and thence, by the small hole, into the atmosphere, without loss by spray. The current had to pass along the whole length of the column of liquid enclosed by the U-tubes, the shorter arms of which enclosed the "intermediate" portions whilst the longer enclosed the portions in which concentration changes had occurred. After electrolysis, the liquid in the outer vessel was removed by means of two wax pipettes of the automatic type, which were thereby washed, then about 20 c.c. were simultaneously removed in the same way from each of the shorter arms of the U-tubes, and analysed as "intermediate" portions. If their concentration differed from that of the original solution by more than the errors of analysis, the experiment was rejected. Finally, the remaining contents of the cathode tube were poured out through the small hole at the top of the longer arm (so that the last portion of the liquid came from the region of the analysed "intermediate" portion) and this was again analysed. In the more dilute solutions the anodic portion was similarly treated but, in the more concentrated solutions, secondary reactions appeared to take place at the anode and therefore this portion was neglected. In all the experiments two cells (marked "*a*" and "*b*" in Table I) were worked in series, one of them having some modifications which need not be described. At first it was found that concentration changes throughout the body of the liquid occurred owing to evaporation, but this was entirely overcome by fitting the cells with loose wax covers bearing on their undersides pads of filter-paper (silica-free) moistened with the same solution as was in use in the cell.

The cells were almost completely immersed in the water of a thermostat kept at 25° ± 0·2° and the solutions all brought to this temperature before filling. The poor conductance of wax, however, made it difficult to compensate for the heating effect of the current,

TABLE I.

Ex. no.		Acid.	Intermediate portions. Cathode.	Intermediate portions. Anode.	Cathode portions. Weight withdrawn (grams.).	Cathode portions. Content in equivs. × 10^3.	Cathode loss in equivs. × 10^3.	Cu deposit in equivs. × 10^3.	T_A.
		C.	*C.*	*C.*					
1	*a*	2·327	2·327	2·327	58·013	133·77	1·30	3·819	0·340
	b		2·320	2·323	29·125	66·55	1·29		0·337
2	*a*	2·328	2·328	2·329	58·161	134·0	1·47	4·371	0·336
	b		2·496	2·329	34·737	79·48	1·46		0·334
3	*a*	1·795	1·801	1·793	50·196	88·47	1·72	4·999	0·344
	b		1·791	1·796	35·182	61·60	1·62		0·323
4	*a*	1·790	1·789	1·795	51·066	89·85	1·66	4·528	0·365
	b		1·792	1·785	35·126	61·60	1·33		0·294
5	*a*	1·313	1·313	1·314	57·510	74·44	1·15	3·586	0·321
	b		1·314	1·314	36·123	46·30	1·18		0·329
6	*a*	0·9957	0·9935	0·9957	49·248	48·27	0·78	2·550	0·306
	b		0·9935	0·9908	36·168	35·24	0·78		0·306
7	*a*	0·7696	0·7698	0·7687	56·513	42·64	0·86	2·922	0·294
	b		0·7695	0·7697	36·370	27·17	0·85		0·283
8	*a*	0·5000	0·4988	0·5019	49·325	24·18	0·50	1·891	0·265
	b		0·5008	0·5005	34·837	16·97	0·46		0·242
9	*a*	0·2688	—	0·2689	56·110	14·60	0·48	2·029	0·238
	b		0·2689	0·2687	35·048	8·95	0·47		0·232
10	*a*	0·1424	0·1429	0·1426	57·586	7·794	0·410	2·004	0·204
	b		0·1423	0·1428	35·247	4·622	0·400		0·200
11	*a*	0·07273	0·07400	0·07240	48·168	3·215	0·283	1·642	0·172
	b		0·07272	0·07300	35·756	2·347	0·250		0·153
	a		anode portions		49·996	3·899	0·268*		0·163
	b		do.		36·217	2·892	0·262*		0·160
12	*a*	0·03274	0·03270	0·03389	52·371	1·501	0·214	1·400	0·153
	b		0·03314	—	35·505	0·978	0·184		0·132
	a		anode portion		49·659	1·838	0·212*		0·151
	b		do.		36·272	1·392	0·205*		0·147
13	*a*	0·01863	0·01868	0·01852	57·800	1·033	0·044	0·329	0·133
	b		0·01873	0·01861	—	—	—		—
14	*a*	0·01969	0·02024	0·01959	62·862	1·270	0·032*	0·267	0·120
	b		0·02141	0·01953	34·569	0·644	0·037		0·137
15	*a*	0·01770	0·01776	0·01778	58·012	0·960	0·071	0·433	0·163
	b		0·01768	0·01784	33·998	0·541	0·063		0·145

* Gain in equivalents : Anode portion analysis.

so this had to be kept down to 10—15 milliamps. Fortunately, the temperature coefficient of transference numbers is small.

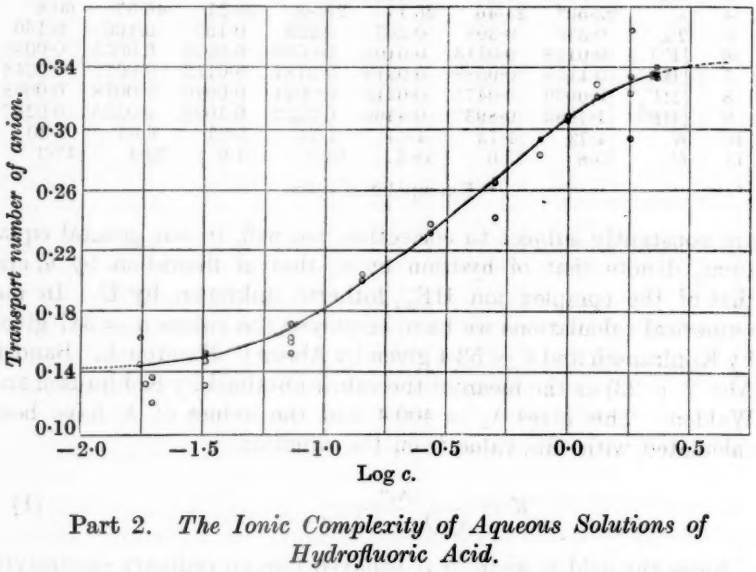
The complete apparatus consisted of two cells, an adjustable electrolytic resistance, milliameter, and two copper coulometers, all connected in series. The coulometers gave almost identical readings, the maximum error in a very unusual case being only 0·5 per cent., so that only the mean is given in Table I.

The duration of each experiment was determined by the concentration. For the dilute solutions, a run of only one hour was allowable if diffusion errors were to be avoided, whilst the most concentrated gave satisfactory results after a run of eight hours.

The results are given in Table I, and Fig. 1 shows graphically the transference number plotted against the common logarithm of the

concentration. The order of accuracy is indicated by the agreement between the different experiments made at the same concentration. The limits are determined essentially by the accuracy of analyses, which is the less the greater the dilution. The principal difficulty was the effect of carbon dioxide, absorbed from the air, on the end-point of the titration.

FIG. 1.



Part 2. *The Ionic Complexity of Aqueous Solutions of Hydrofluoric Acid.*

Aqueous solutions of hydrofluoric acid are very abnormal in their properties, especially with regard to the variation of conductance with concentration. Jaeger (*Z. anorg. Chem.*, 1901, **27**, 22) concluded, from measurements of the solubility of mercuric oxide, that the solution contained mainly double molecules, H_2F_2, whilst Pick (Nernst's "Festschrift," 1912, 360), from conductivity data, was led to postulate the absence of double molecules and the existence of the complex ion, HF_2'. The freezing-point measurements of Paternò and Peratoner (*Atti R. Accad. Lincei*, 1890, [iv], **6**, 306), although they are not at all self-consistent, rather support the latter view, since they give values for i differing but little from 1. Finally, as we shall show, our determinations of the transference numbers of hydrofluoric acid at various concentrations strongly support Pick's hypothesis.

The most trustworthy measurements of the conductivity of hydrofluoric acid solutions, having regard to the purity of the materials, appear to be those of Deussen (*Z. anorg. Chem.*, 1905, **44**, 312),

whose values for the equivalent conductivity, λ, we quote in row 4 of Table II. The value of λ_∞ may be calculated from the mobilities of the simple ions, since the proportion of complex ion must decrease to zero with increasing dilution. As mobilities are quantities which

TABLE II.

1	v	0·5	1	2	4	8	16	32
2	C	2	1	0·5	0·25	0·125	0·0625	0·03125
3	log C	0·3012	0·0000	$\bar{1}$·6990	$\bar{1}$·3979	$\bar{1}$·0969	$\bar{2}$·7959	$\bar{2}$·4949
4	λ	23·50*	24·46	26·17	29·88	36·21	46·37	60·8
5	T_A	0·336	0·308	0·267	0·228	0·193	0·166	0·150
6	[F′]	0·0118	0·0113	0·0104	0·0089	0·0072	0·0055	0·0040
7	[H·]	0·1118	0·0588	0·0319	0·0184	0·0112	0·0072	0·0048
8	[HF_2']	0·0999	0·0475	0·0215	0·0094	0·0040	0·0018	0·0008
9	[HF]	1·7883	0·8937	0·4466	0·2222	0·1098	0·0535	0·0257
10	K_2	4·72	4·72	4·65	4·75	5·03	6·05	7·30
11	U	75·8	73·0	68·3	64·9	61·0	53·4	47·3

* Extrapolated value.

are constantly subject to correction, we will, in our general equations, denote that of hydrion by a, that of fluoridion by b, and that of the complex ion HF_2', hitherto unknown, by U. In our numerical calculations we have employed the values $a = 347$ given by Kohlrausch and $b = 53{\cdot}4$ given by Abegg ("Handbuch," Band 4, Abt. 2, p. 23) as the mean of the values obtained by Kohlrausch and Walden. This gives $\lambda_\infty = 400{\cdot}4$ and the values of K have been calculated with this value from the equation

$$K = \frac{\lambda_v^2}{\lambda_\infty(\lambda_\infty - \lambda_v)v} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Since the acid is weak, if it behaved like an ordinary electrolyte, K should be a constant equal to the mass action constant

$$K_1 = [H^\cdot][F']/[HF] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Actually, K becomes constant ($7{\cdot}4 \times 1{\cdot}0^{-4}$) only at dilutions greater than $v = 64$.

Again, the transference number, calculated from the mobilities, is, for the anion, $53{\cdot}4/(347 + 53{\cdot}4) = 0{\cdot}132$ if the acid ionises simply, and Fig. 1 shows that our figures are compatible with this value for infinite dilution. Moreover, by extrapolation, it is seen that at dilutions greater than $v = 64$ the transport number approaches very closely to this value, so that there can be no appreciable quantity of the complex ion remaining. Consequently, K for these dilutions is a true measure of the mass action K_1, which we may thus write equal to $7{\cdot}4 \times 10^{-4}$.

If now we assume (1) that the only anions are F′ and HF_2' and (2) that there is no appreciable polymerisation to form H_2F_2—

which is supported by freezing-point data, we have the following equations:

$$[H^{\cdot}] = [F'] + [HF_2'] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$C = [HF] + [H^{\cdot}] + [HF_2'] \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where C is the stoicheiometrical concentration determined by titration, and

$$\lambda C = a[H^{\cdot}] + b[F'] + U[HF_2'] \quad . \quad . \quad . \quad . \quad (5)$$

Pick (*op. cit.* and Abegg's "Handbuch," Band 4, Abt. 2, p. 38) assumed a value for U and then solved equations 2, 3, 4, and 5 from a conductivity measurement by Ostwald of the 0·25N-solution. This gave him the data to calculate the second mass action constant,

$$K_2 = [HF_2']/[HF][F'] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

With the value thereby obtained, 5·5, he calculated λ for concentrations over the range $v = 1$ to $v = 64$ and obtained good agreement with the experimental values. He found that the value arbitrarily assigned to U had very little influence on the final figure.

This procedure is not entirely free from objection. Since U was set very nearly equal to b, it may be seen from equations 3 and 5 that the (specific) conductivity is almost strictly proportional to $[H^{\cdot}]$, whilst from equations 2, 3, and 6 we derive

$$[H^{\cdot}]^2 = K_1[HF] + K_2K_1[HF]^2 \quad . \quad . \quad . \quad . \quad (7)$$

For a solution of any given concentration, since the ionisation is small, [HF] is very little affected by the proportion of complex ion which may be present, but this makes its influence felt mainly by the third term (in K_2) associated with the square of [HF]. A 10 per cent. variation in the value of K_2 affects the calculated value of $[H^{\cdot}]$ by only 4·5 per cent. when $C = 1$ and by less than 2 per cent. when $C = 0{\cdot}1$. Since, now, the value of K_2 was chosen to fit the conductivity data at $C = 0{\cdot}25$, it is clear that the agreement found might have occurred even if there had been a considerable change in the real value of K_2 with varying concentration, which would have been incompatible with the theory. In other words, the equation was not sufficiently sensitive to K_2 and hence to the proportion of complex ion present.

The transference number on the contrary is directly sensitive to changes in the nature of the ions. Thus, for the anion, we have

$$T_A = \frac{b[F'] + 2U[HF_2']}{\lambda C} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The factor 2 appears because the complex ion on migration removes a hydrogen atom (which subsequently ionises in the course of titra-

tion) with it in addition to that lost by discharge in compensation for its removal. Consequently T_A is sensitive to $[HF_2']$ even if $U = b$, whilst the conductivity is not.

By combining equations 2, 3, 4, 5, and 8, we obtain the expression

$$[F'] = \frac{p - r}{2b} - \frac{\sqrt{(p-r)^2 - 8bK_1(aC - b)}}{2b} \quad . \quad . \quad (9)$$

where, for brevity, we have $p = (2 - T_A)\lambda C$ and $r = 2K_1(a + b)$. The negative sign in the solution of the quadratic is necessary to fulfil the condition $[F'] \gtrdot [H^*]$.

$$\text{Also} \qquad [H^*] = \frac{p}{2a} - \frac{b}{2a}[F'] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

In equation (10) it may be noticed that, since $b/2a = 0{\cdot}77$ and $[F'] \gtrdot [H^*]$, the concentration of the hydrion can be determined within 8 per cent. from constants, the transference number, the conductivity, and the concentration without knowledge of the concentration of either ion.

Table II gives the experimental values of λ and T_A taken from smoothed curves and the calculated concentrations of the three ions and the undissociated acid. In the tenth row are also given the calculated values of K_2, which is found to be satisfactorily constant except for the very dilute solutions in which $[HF_2']$ is so small that very slight absolute errors make a big proportional difference. The values of U shown in the eleventh row increase steadily with increasing concentration. By the method of calculation adopted, this term is made to bear the accumulated errors of all the others, but so regular a variation suggests some constant error. From the transference number in the most concentrated solution, even assuming a negligible quantity of F', U cannot be less than 70·6, and we may provisionally accept the value 75. It has been found that if the value 50 instead of 53·4 is given to b, the values of U are almost constant at 75 and at the same time the values of K_2 are more constant than as given, having a mean value of 4·4. The absolute values of the concentrations are not materially changed. This point is being made the subject of further investigation, since the mobility of fluoridion cannot be regarded as having been firmly established.

Subject to this small correction, the present work seems to establish definitely the fundamental postulates of Pick and to fix the concentration of the ionic and molecular species in aqueous solutions of hydrofluoric acid.

If we regard the ion HF_2' as coming from the possible acid H_2F_2, the latter must be strong and it is interesting to find $[HF_2']$

giving a constant in a mass action expression. This is in conformity with the work of Bates (*J. Amer. Chem. Soc.*, 1915, **37**, 1421), whose conclusions may be restated in the form that, for strong electrolytes, the activity of the ions is nearly proportional to the molality, though this is not the case for the undissociated molecules.

Summary.

(1) Transport numbers have been determined in solutions of hydrofluoric acid ranging from 0·016 to 2·3 normal.

(2) Pick's assumption that a complex ion, HF_2', is formed by the reaction $HF + F' = HF_2'$ is confirmed.

(3) An approximate value of 75 has been derived for the mobility of hydrofluoridion.

(4) The concentrations of the three ions present in solutions of this range of concentration have been determined.

(5) The value $K_2 = 4·7$ has been derived for the equilibrium constant of the reaction $HF + F' = HF_2'$.

We wish to express our appreciation of the kindness of the Scottish Oil Agency, Ltd., in providing the wax from which the vessels used were made.

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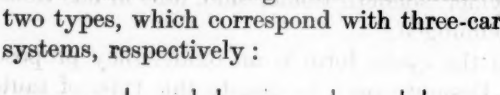
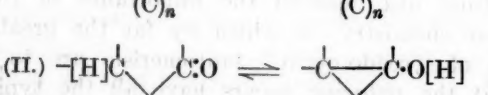
XXXVI.—*Ring-chain Tautomerism. Part IX. The Mutarotation of the Sugars.*

By JOHN WILLIAM BAKER, CHRISTOPHER KELK INGOLD, and JOCELYN FIELD THORPE.

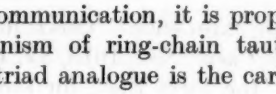
(1) *Introduction.*

IN the preceding parts of this series attention has been directed to the existence of ring-chain tautomeric systems of the following two types, which correspond with three-carbon and keto-enol triad systems, respectively:

(I.)  (Ingold, Perren, and Thorpe, T., 1922, **121**, 1765)

(II.)  (Deshapanda and Thorpe, *ibid.*, p. 1430, and others)

In this communication, it is proposed to consider the occurrence and mechanism of ring-chain tautomeric changes in systems of which the triad analogue is the carboxyl group :

(III.)  (Jacobson and Stelzner, Meyer and Jacobson's "Organischen Chemie," 2 Aufl., 1, 2, 886, 910, 915, 927)

Although cases of this type of ring-chain interchange (III) are very much more numerous than those of the preceding types (I and II), many investigators having been in direct experimental contact with the phenomenon, it is remarkable that the true nature of the change has not hitherto been recognised save by Jacobson and Stelzner, whose *a priori* considerations (*loc. cit.*, p. 886) render the occurrence of mobile systems of the type indicated probable to a high degree. The essence of their views is contained in the following extract from their introduction to the section on hydroxy-aldehydes and hydroxy-ketones.

"Carbonyl-Verbindungen reagiren nun mit Hydroxyl-Verbindungen bekanntlich unter Acetal-Bildung. Es liegt daher der Gedanke nahe, dass in Körpern, deren Moleküle zugleich Carbonyl und alkoholisches Hydroxyl enthalten, diese Gruppen miteinander unter acetalartiger Verknüpfung zuzammentreten. So ist man dazu gekommen, neben den Formeln eigentlicher Aldehyd- und Ketonalkohole für die hier zu behandelnden Verbindungen auch die Struktur von "Halbacetalen" in Betracht zu ziehen, z.B. :

statt $OH\cdot CH_2\cdot CHO$ die Formeln $O<\begin{matrix}CH_2\cdot CH(OH)\\ CH(OH)\cdot CH_2\end{matrix}>O$

" $\begin{matrix}CH_2\cdot CO\cdot CH_3\\ |\\ CH_2\cdot CH_2\cdot OH\end{matrix}$ " " $\begin{matrix}CH_2\cdot C(OH)\cdot CH_3\\ |\quad\quad >O\\ CH_2\cdot CH_2\end{matrix}$

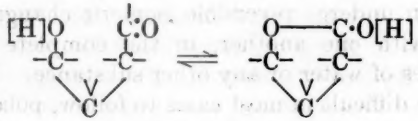
Bei den erstern Beispiel würde es sich um Polymerie handeln, und tatsächlich ist für mehrere einfach α-Oxy-aldehyde in frisch bereiteter wässriger Lösung das doppelte Molekulargewicht gefunden worden. Das zweite Beispiel, in welchem die beiden Formeln miteinander nicht polymer, sondern isomer sind, fällt in das Gebiet der Tautomerie-Erscheinungen."

Since in these cases the cyclic form is an oxide, they proposed the term "Oxo-cyclo-Desmotropie" to denote this type of tautomerism.

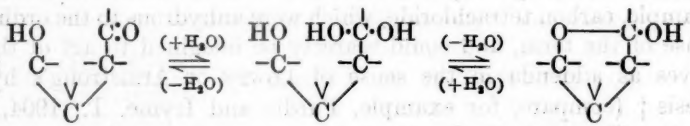
Jacobson and Stelzner also realised the importance of their generalisation in sugar chemistry, in which by far the greatest number of examples of "oxido-cyclo" tautomerism are to be found. The fact that the reducing sugars have all the typical

properties of aldehydes or ketones, whilst their stereochemical relations, their connexion with the glucosides, etc., prove them to be cyclic oxides, is obviously to be traced (*ibid.*, p. 915) to the occurrence in solution of reversible isomeric changes of type (III); whilst the additional circumstance that the cyclic individual can exist in two stereoisomeric modifications which, although not directly interconvertible in ordinary circumstances, can come into equilibrium through the intervention of their open-chain isomeride, is evidently (*ibid.*, p. 915) the root cause of the mutarotation displayed by practically all sugars which contain the necessary grouping.

This simple view of the matter does not, however, appear to have been generally adopted by workers in the sugar group, who, with few exceptions, appear to favour mechanisms which depend on the addition and subsequent removal of water. Two rival theories hold the field. One, suggested by Lowry (T., 1903, **83**, 1316), replaces the simple ring-chain interchange of Jacobsen and Stelzner:

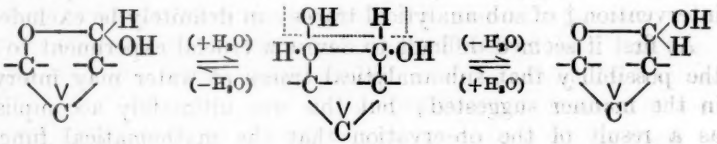
(IV.)  (*α- and β-forms*)

by the sequence of changes:

(V.) 

(*α- and β-forms*)

The second, proposed by E. F. Armstrong (T., 1903, **83**, 1309), excludes the aldehydic individual and postulates the intervention of an oxonium hydroxide:

(VI.) 

(*α-form*) (*β-form*)

(See also p. 285.)

The object of this paper is to endeavour to decide between these three possibilities (IV, V, and VI).

Two methods have been employed. The first consists in attempting to decide by dynamical experiments the crucial point as to

whether water does, or does not, intervene in the manner postulated by Lowry and Armstrong. The second consists in examining the occurrence of mutarotation in cases to which, for structural reasons, one or two of the three suggested mechanisms could not possibly apply. Both methods are based fundamentally on the conviction that the phenomenon is essentially of the same kind throughout, and not, as Irvine and Steele have supposed, of different kinds in different individual cases (T., 1915, **107**, 1239—1240).

(2) *Dynamical Evidence.*

The necessity for assuming that a hydrate intervenes is not obvious. The evident similarity of the oxido-cyclo-change (type III) with the keto-cyclol and three-carbon changes (types I and II) suggests that similar conditions will prevail in all three cases; and it has been shown (Ingold, Perren, and Thorpe, *loc. cit.*) that, comparably with the ketonic and enolic modifications of ethyl acetoacetate, a pair of pure liquid esters related to one another in the manner of the formulæ (I) can undergo reversible isomeric change, and come into equilibrium with one another, in the complete absence of analytical quantities of water or any other substance. For obvious reasons it would be difficult in most cases to follow, polarimetrically or otherwise, the interconversion of pure fused sugars; * but mutarotation has frequently been observed to occur in solvents, for example, carbon tetrachloride, which were anhydrous to the ordinary sense of the term, and could scarcely be imagined to act of themselves as addenda in the sense of Lowry or Armstrong's hypothesis † (compare, for example, Purdie and Irvine, T., 1904, **85**, 1049). The necessity for the intervention of analytical quantities of water is therefore out of the question, but since, according to schemes (V) and (VI), extremely small amounts might be supposed, indeed *have* been supposed (Irvine and Steele, *loc. cit.*), to bring about the change, further evidence is needed before the postulated intervention ‡ of sub-analytical traces can definitely be excluded.

At first it seemed difficult to devise a crucial experiment to test the possibility that sub-analytical traces of water may intervene in the manner suggested; but this was ultimately accomplished as a result of the observation that the mathematical function

* *Note* (added later): See, however, the recently published, important contribution by Riiber (*Ber.*, 1923, **56**, [*B*], 2185), which deserves fuller reference than this mere citation.

† This could scarcely be said of formamide, the mutarotation of glucose in which has been observed by Mackenzie and Ghosh (*Proc. Edin. Roy. Soc.*, 1914, **35**, 22).

‡ See footnote, p. 282.

which in this case would represent the velocity of mutarotation in analytically "dry" solvents possesses notable singularities which could easily be verified by experiment.

In order better to understand the inner meaning of the mathematical analysis which follows, it is desirable in the first place to form a rough mental picture of the process under examination. Let us imagine that in an analytically "dry" solvent relatively large amounts of the α- and β-sugars undergo interconversion through the medium of a hydrate, to the quantity of which a maximal limit is set for all time by the magnitude of the small trace of water originally present. It is conceivable that the dynamics of the process will, broadly, follow the mechanical analogy of a liquid levelling itself in two tanks connected by a narrow pipe; that is to say, any alteration of the conditions which has the effect of widening the channel of communication, for example, increasing the bore of the pipe, or setting a higher limit to the possible quantity of hydrate by increasing the initial trace of water, must expedite the process. This is merely a *prima facie* consideration, and must of course be held subject to mathematical confirmation, and subject to possible modifications arising from other influences.

In developing these considerations, two points, both susceptible of control from experiment, must clearly be distinguished. The first is the *form* of the mutarotation–time curve. The second, quite distinct from this, but depending on it for its numerical expression, is the *spacing out* of a series of mutarotation–time curves each of which corresponds with a different initial concentration of water.

In order to test the hydrate theory on each of these two points, let us, in the first place, state in general terms the dynamical consequences of the mechanism represented by the following chemical equation:

$$H_2O + S_\alpha \underset{(k_2)}{\overset{(k_1)}{\rightleftharpoons}} M \underset{(k_4)}{\overset{(k_3)}{\rightleftharpoons}} S_\beta + H_2O \quad . \quad . \quad . \quad \text{(VII.)}$$

In this equation S_α and S_β denote the α- and β-sugars, respectively, and M denotes the hydrate through the medium of which the interconversion is assumed to occur. Let k_1 and k_4 be the velocity coefficients for the formation of M from the α- and β-sugars, respectively, and k_2 and k_3 the coefficients for the decomposition of M in the two directions. Also, let a be the initial molecular concentration of the α-sugar, and b the initial molecular concentration of water, the initial concentrations of the intermediate complex and of the β-sugar each being zero. After the lapse of

a time t, let the concentration of the α-sugar be $a - x$, and that of the β-sugar y; then the concentration of the complex must be $x - y$, and that of the water $b - x + y$. The following differential equations may now be set up (for a single temperature):

$$dx/dt = k_1(a - x)(b - x + y) - k_2(x - y) \quad . \quad . \quad \text{(i)}$$
$$dy/dt = k_3(x - y) - k_4 y(b - x + y) \quad . \quad . \quad . \quad \text{(ii)}$$

The solution of these simultaneous differential equations of the first order and second degree depends on that of an ordinary differential equation of the second order and third degree. If equation (i) be differentiated, and y and dy/dt be eliminated from (i), (ii), and the differentiated form of (i), we obtain, after all possible simplification, the equation:

$$\frac{d^2x}{dt^2}(Ax + B) + \left(\frac{dx}{dt}\right)^2 C + \frac{dx}{dt}(Dx^2 + Ex + F) + (Gx^2 + Hx + J) = 0 \quad . \quad . \quad \text{(iii)}$$

where the coefficients A, B, . . . J have the values

$$\left.\begin{aligned} A &= -k_1 \\ B &= k_1 a + k_2 \\ C &= k_1 + k_4 \\ D &= k_1(k_1 - k_4) \\ E &= (-2k_1 + k_4)(k_1 a + k_2) - k_1(k_3 - k_4 b) \\ F &= (k_1 a + k_2)(k_1 a + k_2 + k_3) + (k_1 + k_4)k_2 b - k_1 k_4 ab \\ G &= -k_1 b(k_1 k_3 + k_2 k_4) \\ H &= k_1^2 k_3 ab + b(k_1 a + k_2)(k_1 k_3 + k_2 k_4) + k_1 k_2 k_4 b^2 \\ J &= -k_1 k_3 ab(k_1 a + k_2) - k_1 k_2 k_4 ab^2 \end{aligned}\right\} \quad . \quad . \quad \text{(iv)}$$

Now if the initial concentration of water is small, the concentration of hydrate must at all times be small, and we may neglect its contribution to the observed rotation. Under these conditions, x is a linear function of the polarimetric measurements, and therefore equation (iii) should express both the form and the spacing of the mutarotation–time curves.

Setting aside for the moment the question of spacing, let us first consider merely the form of the curves.

The numerical data recorded in this paper, which refer throughout to cases in which the initial concentrations of water were small, show, amongst other things, that in this region the mutarotation curve is uniformly exponential in character, in the sense that a linear function of time is proportional to the logarithm of a linear function of x, within the limits of experimental accuracy. As a matter of fact, reference to the literature shows that the mutarotation curve has the same exponential form, a linear function

of time varying as the logarithm of a linear function of the observed rotation, not only in the region of small concentrations of water, but also outside this region; in fact, over a wide range of variables, including a considerable variety of sugars and solvents. The significance of this wide uniformity will appear in the sequel (p. 279 and p. 282, footnote), but for the present we must confine our considerations to the region within which the possible contribution of the hydrate to the observed rotation is negligible.

This experimental result must mean one of two things. Either the mutarotation curves, that is, the (x, t) curves, are functionally exponential; or, although not functionally exponential, they simulate the exponential form to a degree of approximation which is within the limits of experimental accuracy.

First, let us examine the conditions under which the (x, t) curves could, on the hydrate theory, be functionally exponential, that is the conditions under which

$$\xi - x = \xi e^{-\lambda t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(v)}$$

could be a solution of (iii). Equation (v) represents the most general exponential relationship applicable to the case, since it has to satisfy the conditions $x = 0$ when $t = 0$, and $x = \xi$ when $t = \infty$. It is, of course, identical with the more commonly used form

$$\lambda = \frac{1}{t} \log_e \frac{\xi}{\xi - x} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(vi)}$$

Equation (v) leads to the following equalities

$$\left.\begin{aligned} x &= -\xi e^{-\lambda t} + \xi \\ dx/dt &= \xi\lambda e^{-\lambda t} \\ d^2x/dt^2 &= -\xi\lambda^2 e^{-\lambda t} \\ x^2 &= \xi^2 e^{-2\lambda t} - 2\xi^2 e^{-\lambda t} + \xi^2 \\ (dx/dt)^2 &= \xi^2\lambda^2 e^{-2\lambda t} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad \text{(vii)}$$

Substituting in (iii), we have

$$D\xi^3\lambda e^{-3\lambda t} + (A\xi^2\lambda^2 + C\xi^2\lambda^2 - 2D\xi^3\lambda - E\xi^2\lambda + G\xi^2)e^{-2\lambda t} + (-A\xi^2\lambda^2 - B\xi\lambda^2 + D\xi^3\lambda + E\xi^2\lambda + F\xi\lambda - 2G\xi^2 - H\xi)e^{-\lambda t} + (G\xi^2 + H\xi + J) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(viii)}$$

For equation (v) to be a solution of (iii), (viii) must be an identity, true for all values of t, and, since $\xi \neq 0$ and $\lambda \neq 0$, the following conditions must all be satisfied:

$$D = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ix)}$$

$$(A + C)\lambda^2 - (2D\xi + E)\lambda + G = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(x)}$$

$$(A\xi + B)\lambda^2 - (D\xi^2 + E\xi + F)\lambda + (2G\xi + H) = 0 \quad . \quad . \quad \text{(xi)}$$

$$G\xi^2 + H\xi + J = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xii)}$$

These equations also determine the hitherto unevaluated constants, λ and ξ, which occur in (v), and it is evident, therefore, that the conditions under which (v) can be a solution of (iii) are really prescribed by two relations, namely, (ix), and the eliminant of ξ and λ between the three equations (x), (xi), and (xii).* If possible, let this eliminant be of the form

$$X_0 + X_1 b + X_2 b^2 + \ldots = 0 \quad . \quad . \quad . \quad \text{(xiii)}$$

where X_0, X_1, etc., are functions of a, k_1, k_2, k_3, and k_4 only. Now since we are testing the possibility that all (x, t) curves may be of exponential form (without prejudice to any particular spacing out), equation (xiii) must be satisfied for varying values of b. This can only be the case if all the coefficients X_0, X_1, etc., vanish independently, and hence the equations :

$$X_0 = X_1 = X_2 = \text{etc.} = 0 \quad . \quad . \quad . \quad . \quad \text{(xiv)}$$

combined with $D = 0$ (equation ix) prescribe the *necessary and sufficient* conditions under which, according to the hydrate theory, the (x, t) curves may be of exponential form.

First let us consider the equation

$$X_0 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xv)}$$

Evidently the solutions of this, combined with those of equation (ix), will give *necessary* conditions. By expanding the coefficients in equations (x), (xi), and (xii) in powers of b :

$$\left.\begin{array}{ll} E = E_0 + E_1 b & G = G_1 b \\ F = F_0 + F_1 b & H = H_1 b + H_2 b^2 \\ & J = J_1 b + J_2 b^2 \end{array}\right\} \quad . \quad . \quad \text{(xvi)}$$

it may easily be shown that the eliminant is of the form assumed (xiii), and that the part independent of b, which vanishes by (xv), is

$$G_1(BE_0 - AF_0 - CF_0)^2 + H_1 CE_0(BE_0 - AF_0 - CF_0) + J_1 C^2 E_0{}^2 = 0 \quad . \quad . \quad . \quad \text{(xvii)}$$

The common solutions of this and (ix) are

$$k_1 = k_2 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xviii)}$$
$$k_1 = k_3 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xix)}$$
$$k_1 = k_4 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xx)}$$
$$k_1 = k_4 \neq 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xxi)}$$

Thus there are four alternatively *necessary* sets of conditions under which (v) may be a solution of (iii). To ascertain whether these

* The eliminant can be evaluated in full, but the method here given is considerably shorter and is rendered possible by the properties of the term X_0 in equation (xiii).

are *sufficient*, it is not necessary to evaluate the other coefficients, X_1, X_2, etc., since the sufficiency or otherwise of each set of conditions becomes immediately obvious on substituting in equation (viii). In this way, it is found that whilst (xviii) and (xx) are sufficient as well as necessary, (xix) and (xxi) are not of themselves sufficient but require additional conditions which enable them to be included under (xviii) or (xx) or (xxii):

$$k_2 = k_3 = 0;\ k_1 = k_4 (\neq 0) \quad . \quad . \quad . \quad \text{(xxii)}$$

Thus the alternative *necessary and sufficient* conditions are those of equations (xviii), (xx), and (xxii).

Chemically, however, these conditions are all absurd, since if they were satisfied the reaction could not proceed; that is to say, there are no conditions under which the (x, t) curves could be functionally exponential.

Now let us examine the possibility that the (x, t) curves, although not functionally exponential, yet simulate the exponential form to a degree of approximation which might be within the limits of experimental error.

In the first place, it can be shown by a calculation closely similar to the preceding one that this may happen in either of three cases:

if k_1 and k_2 are small compared with k_3 and k_4 . . . (xxiii)
if k_2, k_3, and $k_1 - k_4$ are small compared with k_1 and k_4 . (xxiv)
if k_1 and k_4 are small compared with k_2 and k_3 . . . (xxv)

These three cases correspond precisely with conditions (xviii), (xxii), and (xx) in the preceding calculation.

Case (xxiii) may be dismissed from inspection, since it represents a non-reciprocal relation between the α- and β-sugars which is opposed to the experimental fact that the mutarotation curve has the exponential form, no matter whether the starting sugar is of the α- or β-variety.

As to case (xxiv), it can easily be shown, for example from equations (i) and (vii), or by inspection of the form of (viii), that the order of λ is determined by k_1 and k_4, and that equation (x) reduces to

$$e^{-\lambda t}(A\xi\lambda + C\xi\lambda - E\xi) + (-A\xi\lambda - B\lambda + E\xi + F) = 0$$

to a first approximation. This can be identically satisfied by choosing appropriate values of λ and ξ. It is easy to prove that the value of ξ is given by

$$\xi = \frac{EB - (A + C)F}{CE} = \frac{a^2}{a - b} \text{ approximately.}$$

That is to say, the quantity of α-sugar changed is either negative or greater than the amount originally taken, which is absurd; hence case (xxiv) is inadmissible.

For the remaining case (xxv), equation (viii) reduces to

$$e^{-\lambda t}(F\xi\lambda - H\xi) + (H\xi + J) = 0$$

to a first approximation. This is identically satisfied if

$$\xi = -\frac{J}{H} = \frac{k_1 k_3}{k_1 k_3 + k_2 k_4} \text{ . } a \text{ approximately . . (xxvi)}$$

and

$$\lambda = \frac{H}{F} = \frac{k_1 k_3 + k_2 k_4}{k_2 + k_3} \text{ . } b \text{ approximately . . (xxvii)}$$

Equation (xxvi) shows that the amount of α-sugar transformed is a positive proper fraction of the amount taken, so that case (xxv) is alone admissible.

Thus calculation shows that although the (x, t) curves cannot, according to the hydrate theory, be functionally exponential, they could, nevertheless, approximate to the exponential form to within the limits of experimental error, provided only that k_1 and k_4 are small enough in comparison with k_2 and k_3. Calculation also shows that, when this occurs, the exponential relationship by means of which the observations can then be represented is of the form (obtained from equations vi and xxvii)

$$\frac{1}{t}\log_e \frac{\xi}{\xi - x} = b \cdot \frac{k_1 k_3 + k_2 k_4}{k_2 + k_3} = bK \text{ . . . (xxviii)}$$

where K is a derived constant depending only on the four velocity coefficients k_1, k_2, k_3, and k_4.

The second of the two points as to which control from experiment can be obtained is in regard to the spacing of a series of mutarotation–time curves, each of which corresponds with a different initial concentration of water; and this, indeed, is the main point which the experiments described in this paper were designed to determine.

It has already been noted that these observations, which refer throughout to the region in which any contribution of a possible intermediate hydrate to the observed rotation must be small, can be expressed, like many other observations both within and without this region, by the exponential relation

$$\frac{1}{t}\log_e \frac{\xi}{\xi - x} = k_{ex} \text{ . . . . . (xxix)}$$

where k_{ex} represents an experimentally determined velocity coefficient. The point of importance is that k_{ex} is found to be very nearly

independent of b, the initial concentration of water; that is to say, different curves corresponding with different concentrations of water are not spaced out, but are practically coincident. Now equation (xxviii) shows that, although the intermediate hydrate theory can accommodate the experimentally found *form* of the mutarotation curve, it imposes on the experimental velocity coefficient, k_{ex}, by the values of which the *spacing* can then be expressed, the form bK; that is to say, k_{ex} should be directly proportional to b and the mutarotation curves for different initial concentrations of water should be spaced out accordingly. The facts are otherwise. Thus dynamics provides a crucial test, the result of which is to show the hydrate mechanism to be untrue for the examples studied.

We may now examine the tautomeric mechanism. According to this view, interchange proceeds, not by the alternate addition and elimination of water, but by the transmigration of a mobile hydrogen atom across the ring-chain system O—. . .—C—O. Thus the α- and β-oxido-sugars must come into equilibrium through the intervention, not of water, but of the open-chain aldo- or keto-modification of the sugar, which may be assumed to be a relatively short-lived phase in the complete tautomeric interchange:

$$S_\alpha \underset{(k'_2)}{\overset{(k'_1)}{\rightleftharpoons}} S_{ALDO} \underset{(k'_3)}{\overset{(k'_4)}{\rightleftharpoons}} S_\beta \quad . \quad . \quad . \quad . \quad \text{(viii)}$$

If k'_1 and k'_4 are the velocity coefficients for the formation of the aldo-phase from the α- and β-sugars, respectively, and k'_2 and k'_3 are the velocity coefficients for its decomposition in the two directions, and if a, x, and y have their previous significance, the governing equations will be

$$dx/dt = k'_1(a-x) - k'_2(x-y) \quad . \quad . \quad . \quad \text{(xxx)}$$
$$dy/dt = k'_3(x-y) - k'_4 y \quad . \quad . \quad . \quad . \quad . \quad \text{(xxxi)}$$

By the process illustrated on p. 273, these equations can be reduced to the form

$$d^2x/dt^2 + (k'_1 + k'_2 + k'_3 + k'_4)dx/dt + (k'_1k'_3 + k'_2k'_4 + k'_1k'_4)x - k'_1(k'_3 + k'_4)a = 0 \quad . \quad . \quad . \quad \text{(xxxii)}$$

the primitive of which is *

* After this paper was written, Dr. Slater Price kindly directed our attention to the fact that equations equivalent to (xxxiii) and (xxxiv) had previously been given by Rakowski (*Z. physikal. Chem.*, 1907, **57**, 321). There had been no intention of claiming any novelty, however, although we were unaware of Rakowski's paper, because the equations given follow at once from the well-known solution of a linear differential equation of the second order, and can, in fact, be written down from inspection.

$$x = Pe^{t/2[\{(k'_1+k'_2+k'_3+k'_4)^2-4(k'_1k'_3+k'_2k'_4+k'_1k'_4)\}^{\frac{1}{2}}-(k'_1+k'_2+k'_3+k'_4)]} + Qe^{-t/2[\{(k'_1+k'_2+k'_3+k'_4)^2-4(k'_1k'_3+k'_2k'_4+k'_1k'_4)\}^{\frac{1}{2}}+(k'_1+k'_2+k'_3+k'_4)]} + \frac{k'_1(k'_3+k'_4)a}{k'_1k'_3+k'_2k'_4+k'_1k'_4} \quad . \quad . \quad \text{(xxxiii)}$$

The last term is evidently the value of ξ. The values of P and Q may be determined by inserting the limit $x = 0$ when $t = 0$, and then differentiating (xxxiii) and inserting the limit $(dx/dt) = k'_1a$ when $t = 0$ (from xxx). Two simultaneous equations then determine P and Q, the values of which are

$$\left.\begin{aligned} P &= \frac{k'_1a[k'_1k'_3+k'_2k'_4+k'_1k'_4-k'_2k'_3-(k'_3+k'_4)^2-(k'_3+k'_4)\{(k'_1+k'_2+k'_3+k'_4)^2-4(k'_1k'_3+k'_2k'_4+k'_1k'_4)\}^{\frac{1}{2}}]}{2(k'_1k'_3+k'_2k'_4+k'_1k'_4)\{(k'_1+k'_2+k'_3+k'_4)^2-4(k'_1k'_3+k'_2k'_4+k'_1k'_4)\}^{\frac{1}{2}}} \\ Q &= \frac{k'_1a[-k'_1k'_3-k'_2k'_4-k'_1k'_4+k'_2k'_3+(k'_3+k'_4)^2-(k'_3+k'_4)\{(k'_1+k'_2+k'_3+k'_4)^2-4(k'_1k'_3+k'_2k'_4+k'_1k'_4)\}^{\frac{1}{2}}]}{2(k'_1k'_3+k'_2k'_4+k'_1k'_4)\{(k'_1+k'_2+k'_3+k'_4)^2-4(k'_1k'_3+k'_2k'_4+k'_1k'_4)\}^{\frac{1}{2}}} \end{aligned}\right\} \text{(xxxiv)}$$

Since the aldo-phase is assumed to be short-lived, k'_1 and k'_4 must be small in comparison with k'_2 and k'_3. Under these conditions, equations (xxxiii) and (xxxiv) reduce to

$$\frac{1}{t}\log_e\frac{\xi}{\xi - x} = \frac{k'_1k'_3 + k'_2k'_4}{k'_2 + k'_3} = K' \quad . \quad . \quad . \quad \text{(xxxv)}$$

to a first approximation. That is to say, the form is exponential, and the spacing zero, in agreement with experiment.

We may now consider the actual experimental results in somewhat greater detail. Allusion has already been made to the numerous measurements which prove the (x, t) curves to be, accurately or very approximately, of exponential form, and references to some of the more extended series of observations are given in section (3) of this paper. Data with regard to the spacing of the (x, t) curves in the region of small concentrations of water have not, however, previously been obtained. A solvent was therefore selected which could be thoroughly dried by exposure for several months to phosphorus pentoxide, so that the concentration of any remaining water must be exceedingly minute; and a sugar was also chosen which was sufficiently soluble in the solvent to render polarimetric observation easily feasible. The velocity of mutarotation of the sugar in the solvent under standard conditions of temperature and concentration was then determined. On applying equation (xxix) to the figures so obtained, it was found to represent them to within the limits of experimental error, the values of k_{ex}

being concordant. The point now to be determined was whether k_{ex} varied with b; for on the hydrate theory the value of the coefficient would depend fundamentally on the minute residual trace of water which, despite the careful desiccation, may be assumed to have remained. The experiment was therefore repeated under the same standard conditions, but with the addition of a known small amount of water. This quantity, although small relatively to the quantity of sugar present, was great in comparison with the minute trace which might not have been removed by the desiccating agent. Several experiments of this kind were carried out, using different small amounts of water within the specified limits as to order of magnitude, and the various values of k_{ex} compared with the concentrations, b_{ex}, of added water, these being practically equal to b (the total water) under the conditions stated. If the reaction were to take place in accordance with the hydrate theories, k_{ex} and b_{ex} should be very nearly proportional; whereas if it should occur without this intervention of water, k_{ex} should be practically independent of b_{ex}.

The distinction between the two cases is well illustrated by the two lines on Fig. 1, on which the main experimental results are also plotted. The ordinates are proportional to k_{ex} and the abscissæ to b_{ex}. Taking the greatest concentration of water as the numerical standard, the theoretical curves connecting k_{ex} and b_{ex} for the two hypotheses are as shown. The results are evidently in agreement with the tautomeric hypothesis, and quite contrary to the view that the interchange takes place through the medium of a hydrate. Indeed the small observed differences in the values of k_{ex}, doubtless representing the usual effect of an admixed solvent, happen to be in the opposite sense to that which the hydrate theory requires.

The numerical data from which Fig. 1 has been drawn are given in the following table. They refer to a 14 per cent. solution of tetra-acetyl glucose in ethyl acetate (dry or moist) at 44·8°.

Proportion by volume of added water ($\propto b_{ex}$) $\times 10^5$.	k_{ex} in reciprocal hours $\times 10^3$.	Period of half-change in hours.
0	22·2	31·2
25	21·1	32·8
50	20·9	33·2
100	20·8	33·2

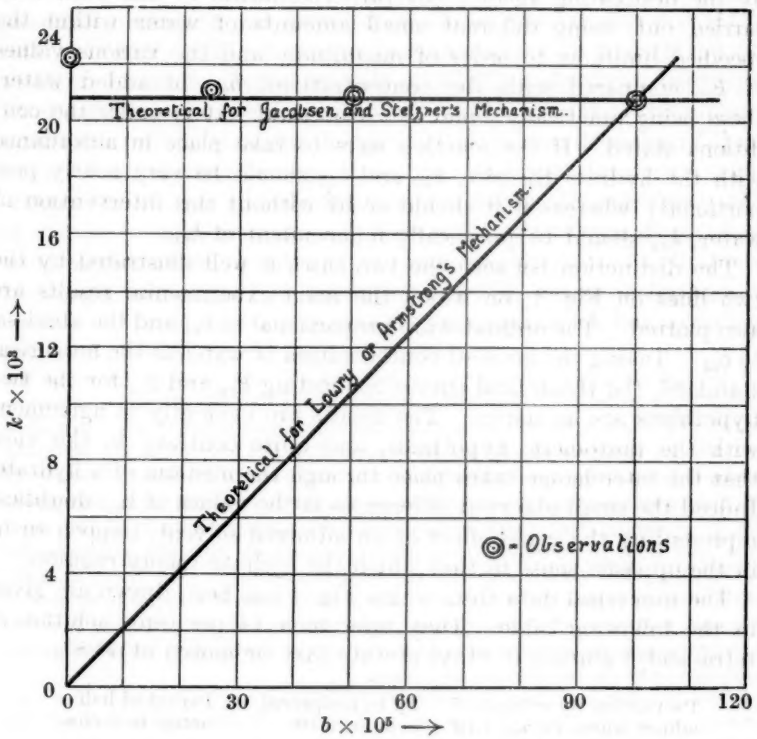
The actual measurements from which these figures are calculated are quoted and discussed in the experimental portion.

In order to obtain a further check, the case was examined in which the molecular concentration of added water is not small in comparison with the initial molecular concentration of water. Since, under these conditions, an appreciable amount of hydrate

might be formed, and since its contribution to the observed rotation is unknown, it is necessary to confine attention to the initial stages of the reaction in which x and $x - y$ are small in comparison with a. Data referring to glucose in methyl alcohol are given in the experimental portion of this paper, in which it is shown that the initial velocity is by no means proportional to the initial concentration of water as the differential equations of the hydrate theory require.

Although, as explained, dynamical considerations lead to an

FIG. 1.



inevitable decision against the hydrate mechanism of mutarotation and in favour of the tautomeric mechanism, it is a more difficult matter to obtain from dynamics alone a distinction between the various types of tautomeric change which might be suggested. Thus the simple change

$$S_\alpha \underset{(k''_2)}{\overset{(k''_1)}{\rightleftharpoons}} S_\beta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ix)}$$

would be governed by the equation

$$dx/dt = k''_1(a - x) - k''_2 x \quad . \quad . \quad . \quad . \quad \text{(xxxvi)}$$

that is to say,

$$\frac{1}{t}\log_e \frac{\xi}{\xi - x} = K'' \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xxxvii)}$$

where

$$K'' = k''_1 + k''_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xxxviii)}$$

From the form of equations (xxxvii) and (xxxviii) it is evident that the kind of experiment which will lead to a clear distinction between the hydrate mechanism (VII) and the tautomeric mechanism (VIII) will not suffice * to decide between the ring-chain mechanism (VIII) and direct geometrical inversion (IX). However, the ring-chain mechanism (VIII) is that to which chemical analogy points, and, in the meantime, the decision between it and mechanism (IX) may well rest on the very significant and definite indications which structural considerations (next section) provide.

In conclusion, then, the evidence afforded by dynamical experiments is clearly to the effect that the mutarotation of sugars is essentially a tautomeric phenomenon, and that neither analytical nor sub-analytical traces of water intervene in the manner suggested by Lowry and Armstrong's hypotheses.†

* Nevertheless, the form of equations (xxxiii) and (xxxiv) opens up the interesting possibility of discovering by polarimetric or refractometric means a case of ring-chain interchange in which the aldo-phase is not short. In such a case, the (x, t) curves should not be exponential, but should be the resultant obtained by adding the ordinates of *two* exponential curves. A study of the mathematical theory shows that it should be possible in a favourable case to evaluate from experimental data the rotatory power of the aldo-form, and then to establish quantitative agreement with the equations for the change, thus confirming the mechanism assumed. We hope at some future date to follow up the matter along these lines if a suitable sugar can be found, but, in view of the general applicability of the exponential function to recorded data for mutarotation, it would appear that sugars with moderately stable aldo-phases are difficult to obtain.

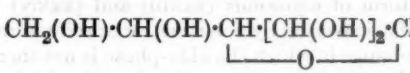
† The possible influence of catalysts in relation to this problem is considered in section (4) of this paper, but we have refrained from discussing the possibility that the special catalytic effect of water might, by a coincidence, exactly counteract the dynamical consequences of the hydrate theory, making them agree with those of the tautomeric theory, and therefore with experiment; because for this to happen, the catalytic influence would have to be negative, a suggestion absolutely contrary to all evidence on the subject. Perhaps it is unnecessary to enlarge further on the obvious fact that nothing in these results touches in any way on the probability, arising from H. B. Baker's classical experiments, that no chemical reaction can take place in the complete absence of water. All that has been shown is that, *if* a trace of water is necessary for mutarotation to occur, it does not act by adding on and splitting off again, as Lowry and Armstrong postulate.

(3) *Structural Evidence.*

The starting point of the considerations of this section is that each of the mechanisms between which we have to discriminate requires the existence of a different molecular grouping as a condition necessary for mutarotation. Thus the tautomeric hydrogen hypothesis (scheme IV) requires the existence of a mobile hydrogen atom and a ring-chain tautomeric grouping O– . . . –C–O or O– . . . –C–N. On the other hand, Lowry's intermediate-hydrate theory (scheme V) is not concerned with any tautomeric grouping, but it requires the existence in the oxide-form of the substance of a hydroxyl group attached to the carbon atom around which the resultant inversion occurs. Then, again, Armstrong's intermediate hydrate theory (scheme VI) requires the existence of a hydrogen atom attached to the carbon atom around which the inversion takes place.

Therefore we may classify the sugars and their derivatives according to the particular theory on the basis of which mutarotation is to be expected :

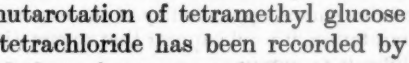
(*a*) Substances which, according to all three theories, should be capable of displaying mutarotation. Examples : *d*-glucose, tetramethyl *d*-glucose, tetra-acetyl *d*-glucose :



(d-*glucose*)

The facts are as follows. The mutarotation of *d*-glucose in water has been measured by Parcus and Tollens (*Annalen*, 1890, **275**, 160), in water and pyridine by Grossmann and Bloch (*Z. ver. deut. Zuckerind.*, 1912, 19), in pyridine by Behrend and Roth (*Annalen*, 1904, **331**, 359), and in formamide by Mackenzie and Ghosh (*loc. cit.*). The mutarotation of tetramethyl glucose in water, benzene, and carbon tetrachloride has been recorded by Purdie and Irvine (*loc. cit.*), and that of tetra-acetyl glucose in water by Fischer and Delbrück (*Ber.*, 1909, **42**, 2778).

(*b*) Substances which should be capable of mutarotation according to the tautomeric hydrogen theory or Lowry's intermediate-hydrate theory, but *not according to Armstrong's intermediate-hydrate theory*. Examples : *d*-fructose, tetramethyl *d*-fructose :



(d-*fructose*)

The mutarotation of *d*-fructose has, however, been observed in water, pyridine, and formamide solutions (Parcus and Tollens, *loc. cit.*; Grossmann and Bloch, *loc cit.*; Mackenzie and Ghosh, *loc. cit.*), and

that of tetramethyl *d*-fructose in water and alcohol (Purdie and Paul, T., 1907, **91**, 289).

(*c*) Substances which should be capable of mutarotation according to the tautomeric hydrogen theory or Armstrong's intermediate hydrate theory, *but not according to Lowry's intermediate-hydrate theory*. Examples: *d*-glucoseoxime, *d*-glucoseanilide, *d*-glucoseimine, *d*-glucosephenylhydrazone, ethylamino-*d*-glucose:

$CH_2(OH)\cdot CH(OH)\cdot CH\cdot[CH(OH)]_2\cdot CH\cdot NH\cdot OH$ (d-*glucoseoxime*. For evidence of constitution, see Irvine and Gilmour, T., 1908, **93**, 1429).

$CH_2(OH)\cdot CH(OH)\cdot CH\cdot[CH(OH)]_2\cdot CH\cdot NH_2$ (d-*glucoseimine*. For evidence of constitution, see Irvine, Thomson, and Garrett, T., 1913, **103**, 238).

However, all these substances exhibit mutarotation (Wohl, *Ber.*, 1891, **24**, 993; Behrend, *Annalen*, 1907, **353**, 106; Irvine and Gilmour, *loc. cit.*; Irvine, Thomson, and Garrett, *loc. cit.*).

(*d*) Substances which should be incapable of mutarotation on all three theories. This class includes the glucosides and all penta-substituted glucoses and fructoses, and it is noteworthy that in none of these cases has mutarotation been recorded, although the interconversion of isomeric forms can sometimes be effected by reagents (KOH, $ZnCl_2$, HCl, etc.). To this point we shall return.

Therefore, the conclusion is that the evidence of structure is definitely in favour of the tautomeric-hydrogen hypothesis and overwhelmingly against both Lowry and Armstrong's modifications of the intermediate-hydrate hypothesis,* for only the first can interpret all the cases in which mutarotation has been observed.

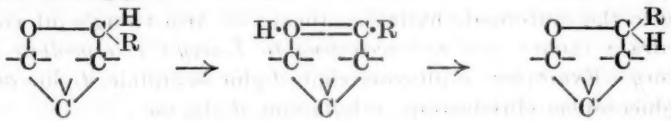
(4) *Isomeric Changes in the presence of Reagents.*

It has been mentioned that the α- and β-forms of substances such as the glucosides and penta-substituted glucoses, which do not undergo mutarotation, can sometimes be converted into one another by reagents. Thus α-acetochloroglucose is converted into the β-form by solid potassium hydroxide (Fischer and Armstrong, *Ber.*, 1901, **34**, 2885), and β-penta-acetyl glucose is converted into the α-form by treatment with anhydrous zinc chloride (Erwig and Konig, *Ber.*, 1889, **22**, 1464, 2207):

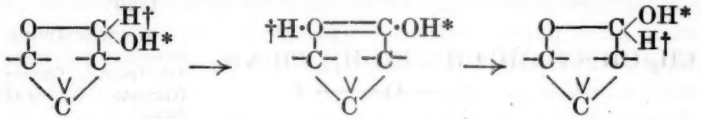
$CH_2(OAc)\cdot CH(OAc)\cdot CH\cdot[CH(OAc)]_2\cdot CH\cdot OAc$

* The same conclusion has recently been drawn by Hirsch and Kossuth (*Fermentforsh.*, 1922, **6**, 302) as a result of the very accurate refractometric investigation which they have carried out on the mutarotation of glucose (see also Riiber, *loc. cit.*).

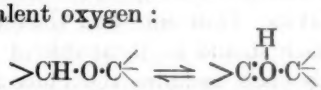
Armstrong (*loc. cit.*) has given an interpretation of such isomeric changes on the basis of an intermediate compound containing quadrivalent oxygen :

(X.) 

It is, however, obvious that this theory cannot escape logical extension to cases in which the group R is OH or NHR′, or NH_2, that is, to substances which show mutarotation in the ordinary sense :

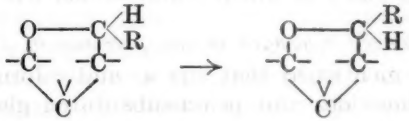
(XI.) 

Apart from an inherent improbability arising from the complete absence of any evidence for the existence of tautomeric ethers containing quadrivalent oxygen :



such a mechanism is untenable on the ground that it fails to explain why mutarotation, in the ordinary sense of the term, ceases when the hydrogen atom marked * is replaced (section 3); it is not *this* hydrogen atom, but *the other one* (marked †), which this theory assumes to be the mobile hydrogen atom. Therefore, scheme (XI) cannot be accepted, and scheme (X) falls with it.

Probably the most reasonable view of these changes which involve the use of powerful reagents is that they are simple geometrical inversions :



The sharp distinction between the character and conditions of occurrence of these changes and the spontaneous changes involving a mobile hydrogen atom may plausibly be referred to a fundamental difference of mechanism, such as the difference between mobile-hydrogen tautomeric change and geometrical inversion.

It may be argued that the necessity for reagents implies the formation of intermediate additive products with the reagents; that catalytic traces of water, or of H˙- or OH′-ions, are possibly necessary for mutarotation, and that hence the difference between the two types of process is more apparent than real, each depending on initial addition to the catalyst. The answer to this is that the

mode of action of catalysts is quite unknown, and that there are other ways in which they may act than by forming intermediate additive products; and, moreover, that, as shown above, the (probably) universal catalyst, water, does not operate in this way so far as concerns the mutarotation of sugars. However, whilst it would serve no useful purpose to enter further into the mode of action, either of the catalytic traces of water, etc., possibly required for mutarotation, or of the powerful reagents which are known to be necessary when the mobile hydrogen atom is lacking, the authors cannot conclude this paper without remarking that, in their view, the method of investigation adopted by Irvine and Steele (*loc. cit.*), who, in a paper entitled "The Mechanism of Mutarotation in Aqueous Solution," describe the effect of adding a reagent (boric acid) which is known or believed to form additive complexes with almost all substances of the sugar series, is likely to complicate rather than simplify the problem. By "the mechanism of mutarotation" is usually meant "the simplest possible mechanism that is of general application," not the complex situation which may arise when a mutarotating substance is deliberately provided with almost limitless possibilities of undergoing reversible or irreversible side-reactions with an added substance.*

EXPERIMENTAL.

(A) *Velocity of Mutarotation of Tetra-acetyl* d-*Glucose in Dry and in Moist Ethyl Acetate.*

Preparation of Tetra-acetyl d-*Glucose.*—Pure anhydrous α-*d*-glucose was acetylated in the usual manner by means of acetic anhydride and sodium acetate, and the penta-acetyl *d*-glucose was carefully purified by crystallisation from dilute alcohol. It was then converted into β-acetobromoglucose by treatment with a saturated solution of hydrogen bromide in acetic acid, and the acetobromoglucose, after being completely purified by crystallis-

* The same remark applies regarding the possible association with water (in the crystalline state or in strongly aqueous solutions) of the components of the ring-chain system. The existence of such hydrates in certain cases can be proved, but that in no way affects the question as to whether they are *structurally necessary* intermediates in the conversion. The whole of the evidence brought forward in this paper goes to show that they are not, but direct dynamical evidence, as obtained in the case of nearly anhydrous solutions, is not possible with strongly aqueous solutions, because we have no means of allowing for the numerous unknown influences (viscosity, radiation-absorption, etc.) which make up what may be termed the normal effect of a variable solvent on the velocity of reactions taking place in it; in nearly anhydrous solvents the normal effect is small, because the change in composition of the solvent is very small (see p. 280 and Fig. 1).

ation from amyl alcohol, was treated with silver carbonate in moist ether as described by Fischer and Delbrück (*Ber.*, 1909, **43**, 2778). The tetra-acetyl *d*-glucose was finally purified by crystallisation from dry ether, and the product stored over phosphorus pentoxide in a vacuum.

Preparation of Dry Ethyl Acetate.—"Pure" ethyl acetate was shaken with anhydrous potassium carbonate and then left in contact with the same substance for several weeks, to remove water and traces of acids. It was then stored over phosphorus pentoxide for a further period of one month, fresh quantities of the oxide being added at intervals, in order to complete the removal of water and convert any traces of alcohol into non-volatile phosphoric esters (Inglis and Knight, P., 1907, **23**, 198). The liquid was then carefully distilled in a dry apparatus containing a long fractioning column, and the middle portion of the distillate stored for use with phosphorus pentoxide in contact with its vapour.

Preparation of Moist Ethyl Acetate.—Since the quantities of water required for the preparation of the moist solutions were too small for direct weighing to be possible, a standard solution of water in dry ethyl acetate was made by weighing, and weighed portions of this were employed. The solution was of about 1 per cent. strength, so that the proportions of water used were known correctly to about 1 part in 10^6—10^7 parts of ethyl acetate, or, 1 part in 10^2—10^4 parts of water added.

Measurements.—The measurements were made in a well-dried 2-dcm. water-jacketed tube, the temperature of the jacket being 44·8° throughout. The polarimeter was a Laurent half-shadow instrument, graduated and fitted with a vernier reading to 5 seconds of arc. A sodium flame was used as a source of illumination.

Results.—Since the solution could not be prepared instantaneously, there was some unavoidable uncertainty regarding the moment at which mutarotation was considered to have commenced ($t=0$). Hence the calculated values of the constant $(1/t)\log_e\{([\alpha_\infty]_D - [\alpha_0]_D)/([\alpha_\infty]_D - [\alpha_t]_D)\}$ were a little irregular in the case of measurements made shortly after starting, for which the proportional error in t would be quite appreciable. Again, the values of the constant calculated from the later readings, for which $[\alpha_t]_D$ is nearly equal to $[\alpha_\infty]_D$, are also subject to error owing to the occurrence of the difference, $[\alpha_\infty]_D - [\alpha_t]_D$ in the denominator of the expression. Therefore, in drawing up the tables quoted below, those readings have been omitted which were obtained earlier than three hours, or later than one hundred hours, from the commencement of each experiment. The further reduction of these results is given in the introductory portion of this paper.

Mutarotation of Tetra-acetyl Glucose.

(*a*) In anhydrous ethyl acetate solution.

Strength of solution = 14·000 grams/100 c.c.

Temp. = 44·8°. $[\alpha_0]_D = 3·15°$. $[\alpha_\infty]_D = 85·0°$.

Time (t hrs.).	α.	$[\alpha]_D$.	$[\alpha_\infty]_D - [\alpha_t]_D$.	$\frac{1}{t}\log_e \frac{[\alpha_\infty]_D - [\alpha_0]_D}{[\alpha_\infty]_D - [\alpha_t]_D}$ (hours^{-1}).
3·37	2° 33′ 1″	9·11°	75·89°	0·02248
3·88	2 44 44	9·80	75·20	0·02190
4·87	3 15 18	11·62	73·38	0·02246
6·00	3 44 55	13·38	71·62	0·02229
6·38	3 54 56	13·96	71·04	0·02223
7·00	4 8 43	14·80	70·20	0·02197
7·33	4 18 5	15·36	69·64	0·02209
9·63	5 8 20	18·35	66·65	0·02135
10·00	5 19 26	19·02	65·98	0·02157
11·05	5 43 2	20·42	64·56	0·02149
12·00	6 7 16	21·87	63·13	0·02166
13·30	6 41 16	23·88	61·12	0·02196
15·00	7 14 52	25·88	59·12	0·02169
16·50	7 47 36	27·83	57·17	0·02175
18·00	8 13 2	29·33	55·67	0·02270
25·80	10 34 38	37·78	47·22	0·02133
27·72	11 13 51	40·10	44·90	0·02166
32·67	12 31 20	44·72	40·28	0·02171
35·42	13 3 21	46·63	38·37	0·02140
47·50	15 29 2	55·28	29·72	0·02128
49·45	15 55 22	56·87	28·13	0·02159
50·63	16 8 41	57·65	27·35	0·02165
53·42	16 36 35	59·30	25·70	0·02169
61·83	17 55 30	63·88	21·12	0·02191
71·20	19 11 36	68·80	16·20	0·02275
75·50	19 56 5	71·18	13·82	0·02356
79·33	20 14 17	72·25	12·75	0·02344
85·25	20 53 37	74·62	10·38	0·02424
96·17	21 34 52	77·03	7·97	0·02422
104·75	21 56 25	78·35	6·65	0·02396

(*b*) In ethyl acetate containing 0·025 per cent. of water.

3·25	2° 22′ 8″	8·44	76·56	0·02062
3·47	2 33 23	9·13	75·87	0·02190
4·87	3 14 35	11·58	73·42	0·02237
6·25	3 51 29	13·78	71·22	0·02229
6·47	3 52 18	13·83	71·17	0·02159
6·88	4 10 30	14·88	70·12	0·02252
7·10	4 17 40	15·34	69·66	0·02273
7·72	4 29 7	16·02	68·98	0·02219
7·97	4 35 18	16·55	68·45	0·02245
10·72	5 38 20	20·15	64·85	0·02174
12·25	6 18 5	22·50	62·50	0·02203
14·25	6 49 0	24·35	60·65	0·02140
14·92	7 6 45	25·40	59·60	0·02128
15·42	7 12 42	25·75	59·25	0·02096
16·58	7 32 3	26·90	58·10	0·02067
17·80	7 50 36	27·95	57·05	0·02028
18·10	7 54 44	28·25	56·75	0·02035
26·17	10 7 5	36·13	48·87	0·01972
27·33	10 32 27	37·63	47·37	0·02001
36·78	12 31 18	44·72	40·28	0·01932
54·33	15 49 56	56·52	28·48	0·01945
60·57	16 58 3	60·56	24·44	0·01995
72·00	18 28 51	65·97	19·03	0·02026
77·33	19 5 26	68·93	16·07	0·02105
84·00	19 53 26	71·03	13·97	0·02105
97·00	20 39 21	73·75	11·25	0·02069

(*c*) In ethyl acetate containing 0·05 per cent. of water.

Time (t hrs.).	α.	$[\alpha]_D$.	$[\alpha_\infty]_D - [\alpha_t]_D$.	$\frac{1}{t}\log_e \frac{[\alpha_\infty]_D - [\sigma_0]_D}{[\alpha_\infty]_D - [\sigma_t]_D}$ (hours^{-1}).
3·25	2° 34′ 38″	9·20°	75·80°	0·02360
4·0	2 51 40	10·22	74·78	0·02262
5·0	3 10 5	11·31	73·69	0·02104
5·47	3 30 22	12·52	72·48	0·02222
7·0	4 14 59	15·17	69·83	0·02270
7·3	4 20 21	15·49	69·51	0·02243
7·53	4 25 46	15·93	69·07	0·02257
8·12	4 39 19	16·62	68·38	0·02213
9·0	4 55 52	17·61	67·39	0·02162
9·67	5 12 15	18·58	66·42	0·02162
10·67	5 27 59	19·52	65·48	0·02094
11·92	5 49 29	20·80	64·20	0·02039
12·50	5 57 42	21·28	63·72	0·02005
15·12	7 11 26	25·68	59·32	0·02131
16·42	7 31 51	26·88	58·12	0·02091
18·65	8 10 9	29·17	55·83	0·02074
19·88	8 33 30	30·57	54·43	0·02054
21·30	8 58 9	31·95	53·05	0·02037
22·83	9 19 58	33·33	51·67	0·02016
24·25	9 39 25	34·48	50·52	0·02086
34·75	12 3 27	43·07	41·93	0·01925
37·67	12 47 24	45·67	39·33	0·01946
39·17	13 15 15	47·33	37·67	0·01982
42·48	13 55 25	49·72	35·28	0·01982
54·75	15 55 51	56·90	28·10	0·01953
56·75	16 18 0	58·20	26·80	0·01980
65·75	17 23 35	62·12	22·88	0·01943
79·0	18 55 56	67·62	17·38	0·01962
89·58	19 45 45	70·57	14·43	0·01938

(*d*) In ethyl acetate containing 0·1 per cent. of water.

3·0	2° 17′ 44″	8·03°	76·97°	0·02057
3·68	2 39 32	9·49	75·51	0·02196
4·08	2 48 7	10·01	74·99	0·02173
4·81	3 10 22	11·49	73·51	0·02235
5·36	3 24 19	12·16	72·84	0·02182
5·93	3 43 8	13·28	71·72	0·02232
6·65	3 56 20	14·06	70·94	0·02157
8·08	4 27 57	15·98	69·02	0·02114
10·16	5 9 58	18·45	66·55	0·02039
10·65	5 31 10	19·70	65·30	0·02123
12·62	6 9 50	22·00	63·00	0·02075
13·75	6 29 15	23·17	61·83	0·02041
14·67	6 48 30	24·32	60·68	0·02047
15·67	7 3 37	25·20	59·80	0·02004
17·17	7 36 23	27·17	57·83	0·02025
26·75	10 25 20	37·22	47·78	0·02014
27·83	10 38 40	38·53	46·47	0·02032
29·50	11 31 52	41·18	43·82	0·02118
37·00	13 16 24	47·40	37·60	0·02103
47·42	15 15 24	54·48	30·52	0·02075
52·50	15 54 56	56·83	28·17	0·02032
54·33	16 12 8	57·85	27·15	0·02032
60·00	17 0 37	60·73	24·27	0·02026
70·75	18 18 37	65·38	19·62	0·02019
81·33	19 15 46	68·78	16·22	0·01991
96·00	20 12 48	72·18	12·82	0·01956

(B) *Initial Velocity of Mutarotation of* d-*Glucose in Dry and in Wet Methyl Alcohol.*

Preparation of Dry α-d-*Glucose.*—"Extra pure anhydrous" *d*-glucose was finely powdered and dried in a slow stream of P_2O_5 dried air, at diminished pressure, and at a temperature of 100°, for four days (compare Mackenzie and Ghosh, *Proc. Roy. Soc. Edin.*, 1914—1915, **35**, 22). It was stored in a vacuum over phosphorus pentoxide.

Methyl Alcohol.—"Absolute" methyl alcohol was treated with a large quantity of clean sodium and then carefully distilled using a fractionating column. It was stored in a bulb with a side tube containing phosphorus pentoxide.

The solutions of water in methyl alcohol were prepared by directly weighing the two materials, but adjustments to the exact quantity of water were made by means of a fine capillary pipette.

Measurements.—The method of making measurements, and the conditions of the determinations were exactly as described on p. 287. The results are tabulated below.

Mutarotation of α-Glucose.

(*a*) In anhydrous methyl alcohol solution.

Strength of solution = 1·2004 grams/100 c.c. Temp. = 44·8°.

Time (hrs.).	α.	$[\alpha]_D$ (degrees).	Time (hrs.).	α.	$[\alpha]_D$ (degrees).
0·25	2° 41′ 7″	111·2	2·63	2° 20′ 40″	97·7
0·43	2 38 10	110·0	4·05	2 7 20	88·4
0·83	2 33 4	106·3	5·53	1 59 47	83·2
1·38	2 30 53	104·8	6·83	1 54 30	79·5

(*b*) In methyl alcohol containing 0·5 per cent. of water.

Strength of solution = 1·2312 grams/100 c.c.

0·28	2° 44′ 43″	111·5	5·85	1° 59′ 0″	80·5
0·72	2 35 25	105·2	6·92	1 53 30	76·8
1·32	2 31 17	102·4	8·38	1 48 0	73·1
1·63	2 25 28	98·5	12·05	1 43 28	69·9
2·22	2 23 11	96·9	23·18	1 35 14	64·5
3·22	2 14 30	91·0	25·08	1 35 14	64·5
4·00	2 8 30	86·9			

(*c*) In methyl alcohol containing 1·0 per cent. of water.

Strength of solution = 1·2172 grams/100 c.c.

0·28	2° 40′ 3″	109·6	4·33	1° 59′ 15″	81·7
0·53	2 36 15	106·9	5·88	1 49 17	74·8
0·88	2 32 15	104·3	8·08	1 41 38	69·7
1·47	2 24 56	99·2	11·42	1 37 29	66·7
1·92	2 20 14	95·9	24·00	1 33 33	64·0
3·22	2 5 18	85·8			

(*d*) In methyl alcohol containing 2·0 per cent. of water.

Strength of solution = 1·2272 grams/100 c.c.

0·28	2° 43′ 25″	110·9	4·22	1° 53′ 14″	76·9
0·52	2 38 20	107·5	5·38	1 46 53	72·6
0·77	2 34 59	105·2	6·75	1 42 38	69·7
1·13	2 27 5	99·9	8·93	1 37 18	66·1
1·82	2 12 40	90·1	11·58	1 34 26	64·1
2·33	2 6 32	85·9	24·25	1 34 26	64·1
3·42	1 57 3	79·5			

Table showing the relation of the initial velocity of the reaction to the amount of water present.

Percentage of water.	dx/dt (graphically) (degrees hours^{-1}).	t (hours).	$[\alpha]_D$ (degrees).	$(a-x)=-([\alpha_\infty]_D-[\alpha_t]_D)$ (degrees.)	$\frac{dx/dt}{a-x}$ (hours^{-1}).
	7·885	0·27	111·6	47·6	0·165
0·0	7·692	0·40	110·4	46·4	0·166
	7·119	0·80	107·3	43·3	0·164
				Mean	0·165
	8·326	0·27	111·2	47·2	0·176
0·5	8·062	0·40	110·0	46·0	0·174
	7·825	0·80	106·6	42·6	0·184
				Mean	0·178
	11·778	0·27	110·6	46·6	0·253
1·0	10·959	0·40	108·7	44·7	0·245
	9·750	0·80	104·6	40·6	0·240
				Mean	0·246
	17·464	0·27	110·8	46·8	0·373
2·0	16·957	0·40	108·6	44·6	0·380
	14·584	0·80	101·8	37·8	0·386
				Mean	0·379

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XXXVII.—*The Isomerism of the Oximes. Part XV. The Alleged Fourth Benzildioxime.*

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ATACK and WHINYATES (T., 1921, **119**, 1184) claim to have obtained a fourth benzildioxime by precipitating with ammonium chloride a solution of α-benzildioxime in dilute sodium hydroxide which had been kept for two hours. The melting point of the product so obtained, to which the authors assigned the prefix δ, is given as 217°, but on drying at 98° this product, it is stated, lost 1·5 per cent.

in weight and the melting point was raised to 220° as compared with 237° for the original α-benzildioxime. The authors were unable to recrystallise the compound, obtaining only α-benzildioxime, and depend for proof of its separate entity on the melting point and the colour of the nickel salt, which they describe as buff-coloured as distinct from the red of the nickel salt of α-benzildioxime.

We have carefully repeated the work of Atack and Whinyates, but have been unable to confirm their results. Considerable difficulty has been experienced, as the description of their experiments is incomplete; for example, it is stated that ammonium chloride converts the new oxime into α-benzildioxime, but in the preparation the amount of ammonium chloride used to precipitate the δ-benzildioxime is not stated; again, no information is supplied as to the composition of the slightly ammoniacal nickel salt solution with which the differently coloured nickel salts were precipitated.

In our attempts to obtain the differently coloured nickel compounds the solutions were prepared by dissolving α-benzildioxime (m. p. 237—238°) in cold 5 per cent. sodium hydroxide in the proportion of 0·5 gram of oxime to 20 c.c. of alkali solution, the proportions and concentrations prescribed by Atack and Whinyates. The solutions were kept at room temperature and at 0° for various periods, two hours, four and a half hours, and six days. Various nickel solutions were employed (A) 5 grams of $NiCl_2,6H_2O$ in 100 c.c. of water; (B) same as (A) with the addition of 5 c.c. of a saturated solution of ammonium chloride and 1 c.c. of concentrated ammonia; (C) same as (A) with 5 c.c. of 2*N*-ammonium hydroxide; (D) same as (A) with 5 c.c. of concentrated ammonia; (E) 5 grams of $NiSO_4,7H_2O$ in 100 c.c. of water with the addition of 5 c.c. of 2*N*-ammonium hydroxide. In (C) and (E) there was a slight permanent precipitate, and in (D) a heavy precipitate, the solution being blue.

Now Atack and Whinyates state "addition of an ammoniacal solution of a nickel salt to a freshly prepared solution of α-benzildioxime in dilute sodium hydroxide solution gives an immediate precipitate of the characteristic red nickel compound, whereas the buff-coloured nickel compound is produced if the solution has been allowed to stand for the necessary time before the addition of the nickel solution." We have found that nickel salts of exactly the same colour were obtained with a freshly prepared alkaline solution of α-benzildioxime and with one which had been kept when any of the above nickel solutions were added, provided the experiments were carried out under comparable conditions. When 2 c.c. of the nickel solution were added to 2 c.c. of the oxime solution, after dilution with an equal volume of water, or *vice versa*, a brick-red

precipitate was invariably obtained. Nickel solutions similar to the above, diluted so as to contain an amount of nickel just sufficient to form the salt gave similar results when 2 c.c. of each solution were mixed.

In certain circumstances, it was found possible to obtain a buff or brown precipitate, particularly when a large excess of nickel solution was present, as was the case when the oxime solution was added drop by drop to the nickel solution. When, however, the equivalent amount of oxime solution had been added, the precipitate, which was at first brown, became brick-red and, as stated above, precipitates of exactly the same colour were obtained with a freshly prepared and with a kept solution of α-benzildioxime.

The effect of alcohol was interesting. Atack and Whinyates say "that the change is not simply from an unstable to a stable nickel compound of the α-benzildioxime is shown by the immediate formation of the stable red nickel compound by the freshly prepared sodium hydroxide solution, especially if alcohol is added to retard the conversion." We have found that alcohol has a marked effect on the colour of the precipitated nickel salt of the oxime. When alcohol was present, the freshly prepared solution gave a much deeper crimson-red precipitate, but exactly the same effect was noticed when alcohol was added to the kept solution immediately before the addition of the nickel solution, or if the nickel solution was mixed with alcohol and the kept solution added to it.

We have also been unable to obtain the low-melting product by precipitation of a kept alkaline solution of α-benzildioxime by means of ammonium chloride, using either about double or slightly less than the amount required to interact with the sodium hydroxide present. The precipitated oxime, after drying as rapidly as possible on a porous tile, melted 3° or 4° lower than the original α-benzildioxime instead of 20° lower as described by Atack and Whinyates; the lowering of the melting point by a few degrees is probably due to the difficulty of rapidly drying the very finely divided compound. The precipitated oxime, when dissolved in alcohol and treated with nickel solution (C), gave the same crimson-red precipitate as a freshly prepared alcoholic solution of α-benzildioxime. We have tried many variations in procedure, but without obtaining any indication of the existence of the fourth isomeride.

We fully realise that negative evidence is unsatisfactory, but we feel it necessary to place on record our failure to confirm the results of Atack and Whinyates, as the former, on the strength of the supposed isolation of the fourth benzildioxime, discards the Hantzsch-Werner theory and proposes a structural theory to account for the isomerism of the oximes (T., 1921, **119**, 1175). On this theory, he

professes to explain all the phenomena associated with the isomerism of the oximes and considers that the stereochemical hypothesis is unnecessary and finds no support in experiment. His theory is essentially that of Beckmann (*Ber.*, 1889, **22**, 1531), who originally suggested the formulæ RR′C:N·OH and RR′C$\overset{\diagdown}{\underset{\diagup}{}}O\overset{\diagdown}{\underset{\diagup}{}}$NH for the isomeric oximes, with the addition of a third unstable structure, RR′C:N$\leqslant^{\mathrm{H}}_{\mathrm{O}}$, to which the name "nitrone" is given. The so-called nitrone structure was suggested by Forster and Holmes (T., 1908, **93**, 244) for the methyl ether of *iso*nitrosocamphor, by Angeli, Alessandri, and Aiazzi-Mancini (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 546) for the *N*-phenyl ethers of the oximes, and by one of us (T., 1914, **105**, 2104) as a tautomeric form of the sodium salts of the isomeric oximes. The question of a tautomeric nitrone form of the oximes was further developed by us (T., 1916, **109**, 650) in an attempt to explain the mechanism of isomeric change in oxime derivatives.

It is, of course, possible that the tautomerides may have a separate existence and the isolation of a fourth benzildioxime would not necessarily invalidate the stereochemical hypothesis as extended by us in our previous papers, but no purely structural theory has been advanced which will account for all the facts. Exigencies of space render a detailed criticism of Atack's views undesirable, particularly as they are open to most of the objections raised to the old structural theory of Beckmann, but a few points may be mentioned. First, it has already been pointed out by Thomas and one of us (T., 1922, **121**, 2102) that Atack has tried to circumvent the objection to the purely structural theory raised by the action of phenylcarbimide on the isomeric oximes by a total misunderstanding of our results and conclusions. Secondly, no structural theory accounts for the failure to obtain isomeric ketoximes from symmetrical ketones, neither does it offer any clue to the different behaviour of the isomeric unsymmetrical ketoximes or of the isomeric benzildioximes in the Beckmann rearrangement. Thirdly, Atack states "the structural theory of the isomerism of the oximes admits the possible existence of only one *O*-ether derived from the so-called *anti*-oxime," and implies that there is no trustworthy evidence for the existence of two isomeric *O*-ethers.

Now two crystalline methyl ethers, besides the *N*-ether, have been obtained from *m*- and *p*-nitrobenzaldoximes (Goldschmidt, *Ber.*, 1890, **23**, 2173; Goldschmidt and Kjellin, *ibid.*, 1891, **24**, 2548, 2553); in other cases, where one isomeride is an uncrystallisable oil, the evidence is admittedly less conclusive. In the case of

m-nitrobenzaldoxime, the ether obtained by the action of methyl iodide on the sodium salt of the *anti*-oxime is given as melting at 63° (Goldschmidt, *loc. cit.*); the *N*-ether, obtained by the action of methyl iodide on the sodium salt of the *syn*-oxime, melts at 117° and with hydriodic acid gives methylamine; the third ether, obtained by the action of methyl iodide on the silver salt of the *syn*-oxime, is given as melting at 69°, although we have found (T., 1913, **103**, 1622) that when pure it melts at 74°. The two ethers, melting according to Goldschmidt at 63° and 69°, differ in crystalline form and on admixture melt in the neighbourhood of 40°; the higher-melting compound on solution in ether and the passage of a small quantity of hydrogen chloride is converted into the lower-melting compound. Goldschmidt and Kjellin found that in the case of the ethers of *p*-nitrobenzaldoxime a similar state of affairs existed, and further, by heating the ethyl ether obtained from the silver salt of the *syn*-oxime with alcohol in a sealed tube and obtaining *p*-nitrobenzamide, demonstrated that the alkyl group was not attached to nitrogen. We have, moreover, repeated more than once and fully confirmed much of this work (T., 1913, **103**, 1625), and the great ease of transformation of the *syn*- into the *anti*-*O*-methyl ether by a trace of hydrogen chloride, a reaction which we have confirmed in a number of instances, is strong presumptive evidence that the alkyl group in the former compounds is attached to oxygen. It has also been shown that the absorption spectra of the isomeric *O*-ethers bear the same relation to one another as do those of the two oximes, whilst they are distinct from that of the *N*-ether (Brady, T., 1914, **105**, 2112). Still further evidence has been obtained by the formation of both *O*-ethers of *m*-nitrobenzaldoxime, one, however, only in small quantity, by the action of α-methylhydroxylamine hydrochloride on *m*-nitrobenzaldehyde and by the conversion of the *O*-methyl ether of *m*-nitrobenz*anti*aldoxime into its isomeride by the action of ultra-violet light. These results and others will be made the subject of further communications.

In addition, pairs of *O*-benzyl ethers of definite melting points have been prepared from the isomeric ketoximes obtained from phenyl *p*-tolyl ketone (Hantzsch, *Ber.*, 1890, **23**, 2330), *p*-chlorobenzophenone (Demuth and Dittrich, *Ber.*, 1890, **23**, 3613), *p*-bromo- and *p*-methoxy-benzophenone (Schafer, *Annalen*, 1891, **264**, 155), and *m*-bromobenzophenone (Kottenham, *ibid.*, p. 173). In every case, these compounds were treated with hydriodic acid and found to give benzyl iodide, indicating that the benzyl group was attached to oxygen.

Recently, Mills and Schindler (T., 1923, **123**, 312), following up the work of Mills and Bain (T., 1910, **97**, 1866), have shown that

Hantzsch's fundamental postulate was correct, namely, that in the doubly-linked tervalent nitrogen atom the valency directions do not lie in one plane. We believe, therefore, that the solution of the problems involved in oxime isomerism lies in the extension of the stereochemical hypothesis rather than in its rejection.

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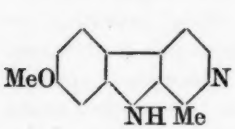
XXXVIII.—*The Methoxyindoles and their Derivatives.*

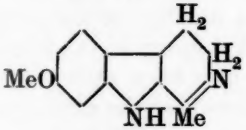
By KENNETH GUY BLAIKIE and WILLIAM HENRY PERKIN, jun.

INTRODUCTION.

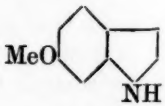
THE investigation of the constitution of harmine (I) and of harmaline (II) (compare Kermack, Perkin, and Robinson, T., 1922, **121**, 1872) has established the fact that these substances are derivatives of 6-methoxyindole (III), and during the course of that work 6-methoxyindole was synthesised and submitted to a detailed examination (*loc. cit.*, p. 1879; T., 1921, **119**, 1632).



(I.)



(II.)



(III.)

The investigation of this substance and its derivatives has brought to light several interesting and novel observations and therefore it seemed desirable that the other isomeric methoxyindoles, containing the methoxy-group in the benzene nucleus and none of which was known, should be prepared and submitted to as exhaustive an examination as possible. This has now been done and the results obtained during the course of this long investigation are described and discussed in the present communication. In order to make the scope of this work clear, and for the sake of brevity, this introduction is divided into the following sections :

I. The Methoxyindole- and Methoxyscatole-2-carboxylic Acids.
II. The Methoxyindoles and Methoxyscatoles.
III. The Methoxyindolealdehydes and Methoxychloroquinolines.
IV. The Acetalylamides, Carbolines, and Indolediazines derived from the Indole- and Scatole-2-carboxylic Acids.
V. The Methoxy-2-nitrophenylacetic Acids.
VI. The 2-Nitro-α-methoxycinnamic Acids.